

TABLE I  
 MAGNETIC MOMENTS OF THE COMPLEXES

Compound	Temp., °K.	$\mu_{\text{eff}}$ , B.M.	
		Found	Lit.
Mo(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	302	3.82	3.80 <sup>a</sup>
Mo(C <sub>5</sub> H <sub>4</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>	302	3.76	...
Cr(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	299	3.7 ± 0.15 <sup>b</sup>	3.86 <sup>c</sup>
Fe(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	299	5.7 ± 0.15 <sup>b</sup>	5.95 <sup>d</sup>

<sup>a</sup> Computed from the *g* values for Mo(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> in Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> reported by Jarrett.<sup>5</sup> <sup>b</sup> Obtained from proton magnetic resonance shifts of solutions; see Experimental section. <sup>c</sup> From ref. 5. <sup>d</sup> From L. Cambi and S. Szego, *Ber.*, **64**, 2591 (1931).

corrections were made using Pascal's constants.<sup>10</sup> The results are recorded in Table I.

**X-Ray Powder Patterns.**—These were recorded with standard equipment using MoK $\alpha$  radiation for In(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> and CuK $\alpha$  radiation for the other compounds. For Mo(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>, the following *d* values, in Å., and relative intensities of lines were found: 8.34 m, 7.90 m, 7.50 s, 2.98 vw, 6.61 ms, 6.07 ms, 5.27 m, 4.11 mw, 3.85 w, 3.78 ms, 3.52 vw, 3.25 w, 2.92 w, 2.85 w, 2.70 w, 2.61 vw, 2.49 vw, 2.37 vw, 2.30 vw, 2.10 vvw, 2.03 vvw (v, very; w, weak; m, medium; s, strong).

(10) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, pp. 91–95.

 TABLE II  
 PRINCIPAL INFRARED ABSORPTION BANDS (CM.<sup>-1</sup>) OF THE COMPLEXES OBSERVED IN CCl<sub>4</sub> SOLUTION

Fe(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub> <sup>a</sup>	Cr-	Mo-	Cr-	Mo-
	(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub> <sup>b</sup>	(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	(C <sub>5</sub> H <sub>4</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>	(C <sub>5</sub> H <sub>4</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>
1572	1578	1563	1603	1582
1526	1523	1521	1530	1522
1425	1435	1431	1445	1432
1390 (1365 sh)	1390	1378	1364	1366
1276	1280	1273	1303	1302
1190	1195	1195	1226	1230
1022	1025	1022	1203	1204
930	932	932	1158	1159
663	682	673	1141	1140
654	662	655	...	...
			1017	1015
			953	947
			867	868

<sup>a</sup> Data from K. Nakamoto, *et al.*, *J. Am. Chem. Soc.*, **83**, 1066 (1961), where assignments are proposed. <sup>b</sup> These data are in good agreement with those of Nakamoto (footnote a) for Cr-(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>.

**Infrared Spectra.**—These were measured on a Perkin-Elmer Model 21 spectrophotometer equipped with a rock-salt prism. Solutions of the molybdenum compounds were prepared and loaded into nitrogen-flushed cells in a nitrogen atmosphere.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA, AND CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

## The Reaction of Pyridine with Cobalt(II) Acetylacetonate in Benzene. Evidence for a Polymeric Species<sup>1</sup>

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The reaction of pyridine with anhydrous cobalt(II) acetylacetonate has been studied spectrophotometrically in oxygen-free benzene. Evidence is presented for species containing cobalt to pyridine ratios of 2:1, 1:1, and 1:2. The species [Co(AA)<sub>2</sub>]<sub>2</sub>py has been isolated from the system. Equilibrium constants for the formation of Co(AA)<sub>2</sub>py and Co(AA)<sub>2</sub>(py)<sub>2</sub> have been determined. Visible spectra for these species as well as [Co(AA)<sub>2</sub>]<sub>2</sub>py and Co(AA)<sub>2</sub> are presented and discussed.

### Introduction

In a series of papers,<sup>2</sup> the intermolecular association of nickel(II) acetylacetonate in hydrocarbon solutions was definitely established. The premise that an oxygen on chelating ligands may act to bridge two Ni(AA)<sub>2</sub> units was given additional support by the isolation<sup>2</sup> of [Ni(AA)<sub>2</sub>]<sub>2</sub>py from the reaction of pyridine with anhydrous [Ni(AA)<sub>2</sub>]<sub>3</sub> in benzene. It is becoming apparent that intermolecular association of this type has given rise to many of the so-called "anomalous" magnetic and spectral properties of neutral chelate complexes of nickel(II).<sup>3</sup> The spectrophotometric titra-

tion of Ni(AA)<sub>2</sub> with pyridine in benzene<sup>2</sup> suggested the absence of any stable 1:1 adducts of pyridine with Ni(AA)<sub>2</sub>, unlike the reaction<sup>4</sup> of pyridine with Cu(AA)<sub>2</sub>.

The possibility that intermolecular association may generally occur with  $\beta$ -diketonate complexes of bivalent transition metals is currently being examined in view of the recent work with nickel. Cotton and Holm<sup>5</sup> suggested that spin-free ( $\mu_{\text{eff}} = 4.8\text{--}5.0$  B.M.) complexes of cobalt(II) with singly charged anionic ligands of the acetylacetonate type may be planar. The structural arguments based on spectral and magnetic properties alone have since been shown to be subject to question by the isolation and structural determination of tetrahedral cobalt(II) dipivaloylmethide.<sup>6</sup> Moreover, it was shown recently that some

(1) This work was presented, in part, at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J. Inquiries should be directed to the author at Case Institute of Technology.

(2) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962), and references therein.

(3) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962), and references therein; but see also R. H. Holm and K. Swaminathan, *ibid.*, **2**, 181 (1963).

(4) D. P. Graddon, *Nature*, **183**, 1610 (1959); W. R. Walker, *Australian J. Chem.*, **14**, 161 (1961).

(5) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(6) F. A. Cotton and R. H. Soderberg, *ibid.*, **84**, 873 (1962).

high-spin salicylaldehyde complexes of cobalt(II) are tetrahedral.<sup>7</sup>

The interaction of pyridine with anhydrous  $\text{Co}(\text{AA})_2$  has been assumed to form the six-coordinate species  $\text{Co}(\text{AA})_2 \cdot (\text{py})_2$ . A similar species, dipyridine-bis-(N-phenylsalicylaldehyde)-cobalt(II), has been isolated by Sacconi, *et al.*<sup>7</sup> They have suggested that this species is in equilibrium with the four-coordinate unsolvated species in pyridine. To establish the presence or absence of polymerized  $\text{Co}(\text{AA})_2$  species, the reaction of anhydrous  $\text{Co}(\text{AA})_2$  with pyridine in benzene was studied spectrophotometrically.

### Experimental

Cobalt(II) acetylacetonate was prepared according to literature methods<sup>5</sup> and triply sublimed. Solutions of  $\text{Co}(\text{AA})_2$  in oxygen-free benzene were prepared by diluting appropriate aliquots of a solution containing a known concentration maintained under dry nitrogen. Aliquots were delivered from an automatic buret. Known amounts of pyridine were added, also under nitrogen, from a stock solution of pyridine in benzene. Fifty-ml. solutions were prepared and the visible spectra from 800–400  $\text{m}\mu$  were observed using a 10-cm. quartz cell, at 25°, with a Cary Model 11 spectrophotometer.

Benzene and pyridine used in this study were purified, as reported previously,<sup>2</sup> and thoroughly flushed with dry nitrogen for 24 hr. prior to use. The commercial pyridine (Brothers reagent grade) was analyzed for water prior to distillation and was found to contain only 0.29 mg./ml. Only the center cut, b.p. 115°, from a distillation over Linde Molecular Sieves was retained.

**Pyridine-tetrakis-(2,4-pentanedione)-dicobalt(II).**—This material was prepared in a manner analogous to the preparation<sup>2</sup> of  $[\text{Ni}(\text{AA})_2]_2\text{py}$ . The crude product was placed in a vacuum desiccator and maintained at oil pump pressures for 24 hr. at 25°; 2.3% nitrogen was found by analysis. The red material crystallized slowly over a 5-day period from a benzene-petroleum ether solution at 0°.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{38}\text{O}_8\text{N}_2\text{Co}_2$ : C, 51.6; H, 5.6; N, 2.4. Found: C, 48.9; H, 5.6; N, 2.1.

**Molecular Weight Measurements.**—The molecular weight of  $\text{Co}(\text{AA})_2$  in oxygen-free benzene was determined at 37° with a Mechrolab, Inc., vapor pressure osmometer, Model 301A, calibrated with biphenyl and bis-(dipivaloylmethano)-Cu(II). A concentration dependence was observed over the range from  $5 \times 10^{-1}$  to  $3 \times 10^{-2}$   $M$  in which the molecular weight varied from 601 to 708, with a reproducibility of  $\pm 1\%$ . These results were obtained by Dr. I. D. Chawla.

### Results

The spectral titration of  $\text{Co}(\text{AA})_2$  with pyridine gave a rather complicated set of curves which (in part) is presented in Fig. 1. With increasing pyridine concentration a general increase was observed in the molar extinction,  $\epsilon_{\text{ob}}$ , to  $C_{\text{py}}/C_{\text{T}} \cong 0.5$  (a,b,c) followed by a general decrease in  $\epsilon_{\text{ob}}$  (d,e,f,g,h) at larger pyridine ratios. From  $C_{\text{py}}/C_{\text{T}} = 0.5$  to  $\sim 10$  (c,d,e) an isosbestic point appears to occur near 470  $\text{m}\mu$ . From  $C_{\text{py}}/C_{\text{T}} \cong 15$  to a 50% pyridine solution (f,g,h) apparent isosbestic points are found at  $\sim 460$  and  $\sim 490$   $\text{m}\mu$ .

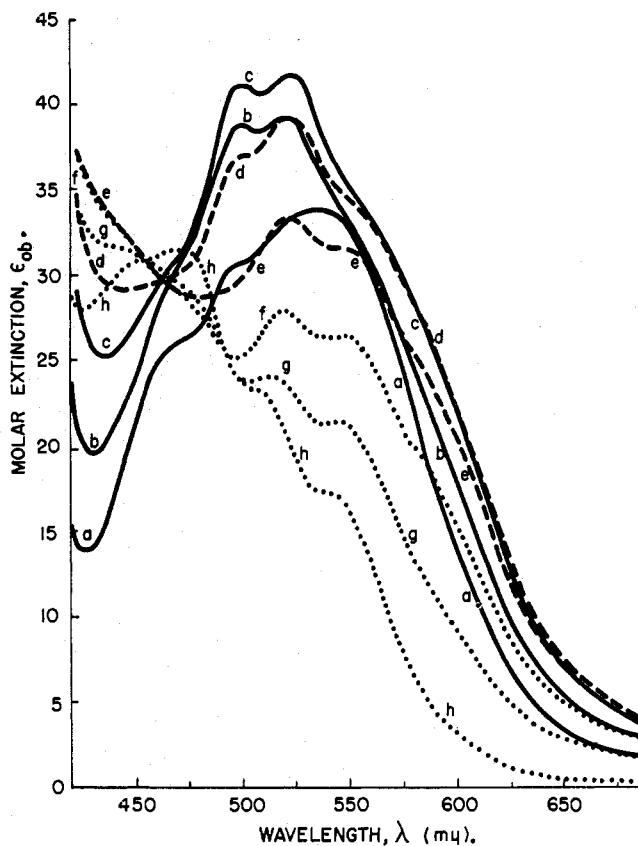


Fig. 1.—The spectrum of  $\text{Co}(\text{AA})_2$  in benzene with various concentrations of pyridine,  $C_{\text{T}} = 4.88 \times 10^{-3} M$ : a, no pyridine; b,  $1.88 \times 10^{-3} M$ ; c,  $3.77 \times 10^{-3} M$ ; d,  $7.06 \times 10^{-3} M$ ; e,  $14.1 \times 10^{-3} M$ ; f,  $23.5 \times 10^{-3} M$ ; g,  $47.1 \times 10^{-3} M$ ; h, 50%.

The spectrum of anhydrous  $\text{Co}(\text{AA})_2$  in oxygen-free benzene is very slightly concentration dependent over the range from  $\sim 5 \times 10^{-2}$  to  $\sim 10^{-3} M$ . This concentration dependence is due to intermolecular association<sup>9</sup> of the  $\text{Co}(\text{AA})_2$ . The changes are small enough, however, to permit the assumption that the various  $[\text{Co}(\text{AA})_2]_n$  species present have identical visible spectra.<sup>10</sup> The molar extinctions observed at various wave lengths are given in Table I.

The changes observed in the spectrum of  $\text{Co}(\text{AA})_2$  as a function of the pyridine concentration cannot be described by considering only equilibria involving various  $[\text{Co}(\text{AA})_2]_n$  species and  $\text{Co}(\text{AA})_2(\text{py})_2$ . At least three species containing pyridine are present with  $0.5 \leq C_{\text{py}}/C_{\text{T}} \leq \infty$ . By plotting  $\epsilon_{\text{ob}}$  vs.  $C_{\text{py}}/C_{\text{T}}$  at various wave lengths (Fig. 2), it was possible to determine the species present and calculate equilibrium constants for the reactions. A total of nine wave lengths were used in analyzing the data and checking the results obtained.

At various wave lengths (see Fig. 2), definite breaks are observed near  $C_{\text{py}}/C_{\text{T}} = 0.5$ . This indicates

(9) The author is grateful to Professor F. A. Cotton, M.I.T., for disclosing some spectral and molecular weight data over a larger concentration range wherein definite concentration dependence is observed.

(10) This assumption is supported by the apparent linearity of the change in absorbance with increasing pyridine to  $C_{\text{py}}/C_{\text{T}} = 0.5$  (*vide infra*). Furthermore for  $n \geq 2$ , it is reasonable to assume the local symmetry surrounding the  $\text{Co}^{+2}$  is not changed drastically with increasing  $n$ . Molecular weight data give an average value of  $n$  greater than 2 in these solutions.

(7) L. Sacconi, M. Ciampolino, F. Maggio, and F. P. Cavalasno, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

(8) For presentation of the data, the following quantities are defined:  $C_{\text{T}}$  is molar concn. of  $\text{Co}(\text{II})$ ;  $\epsilon_{\text{ob}} = A/lC_{\text{T}}$ , where  $A$  is absorbance,  $l$  is path length;  $f_i$  is the fraction of species  $i$ ,  $\sum f_i = 1$ ;  $C_{\text{py}}$  is total molar concentration of pyridine;  $(\text{py})$  is the molar concentration of uncomplexed pyridine.

TABLE I  
 OBSERVED EXTINCTION AT VARIOUS WAVE LENGTHS FOR THE REACTION OF  $\text{Co}(\text{AA})_2$  WITH PYRIDINE IN BENZENE

Concn. $\text{Co}(\text{II})$ $M$	$C_{\text{py}}/C_{\text{T}}$	$\epsilon_{\text{ob}}$ at $\lambda$ ( $m\mu$ )									
		425	444	465	491	503	525	540	575	625	
$4.84 \times 10^{-3}$	0	13.9	18.6	25.9	30.0	30.9	33.7	34.0	25.0	6.97	
	0.199	17.8	19.6	27.2	34.3	35.7	37.0	35.3	25.9	8.6	
	0.389	20.5	21.8	29.8	37.4	38.7	39.1	35.6	26.7	9.6	
	0.584	25.1	24.0	29.8	38.6	40.4	40.6	36.7	27.7	11.2	
	0.779	28.4	26.1	30.5	39.3	41.1	42.0	38.0	30.4	13.4	
	1.17	31.7	28.2	30.3	37.4	39.4	41.0	37.0	30.1	13.2	
	1.46	33.3	29.3	30.0	35.4	37.2	39.4	36.0	29.8	13.0	
	1.95	36.1	31.5	29.9	33.1	34.7	37.4	35.2	29.5	12.8	
	2.93	37.2	33.0	29.7	29.2	30.5	33.3	31.8	26.9	12.1	
	4.86	37.2	33.0	29.7	26.0	25.7	27.8	26.5	21.0	8.6	
$2.90 \times 10^{-3}$	0	18.3	18.3	29.5	29.5	30.3	34.7	35.7			
	0.083	19.6	19.6	32.0	32.0	32.4	36.2	36.1			
	0.165	20.2	20.2	33.7	33.7	34.3	37.0	36.3			
	0.248	20.9	20.9	35.5	35.5	36.1	38.3	36.3			
	0.330	22.1	22.1	37.2	37.2	37.6	39.2	37.5			
	0.495	23.6	23.6	38.3	38.3	40.1	41.0	37.7			
	0.660	24.2	24.2	38.8	38.8	40.1	41.0	37.1			
	0.823	25.0	25.0	37.3	37.3	39.5	40.6	36.7			
	1.15	27.0	27.0	36.4	36.4	38.6	40.2	36.7			
	1.65	29.0	29.0	33.8	33.8	36.1	39.1	35.5			
2.47	31.1	31.1	30.6	30.6	32.8	36.4	34.1				

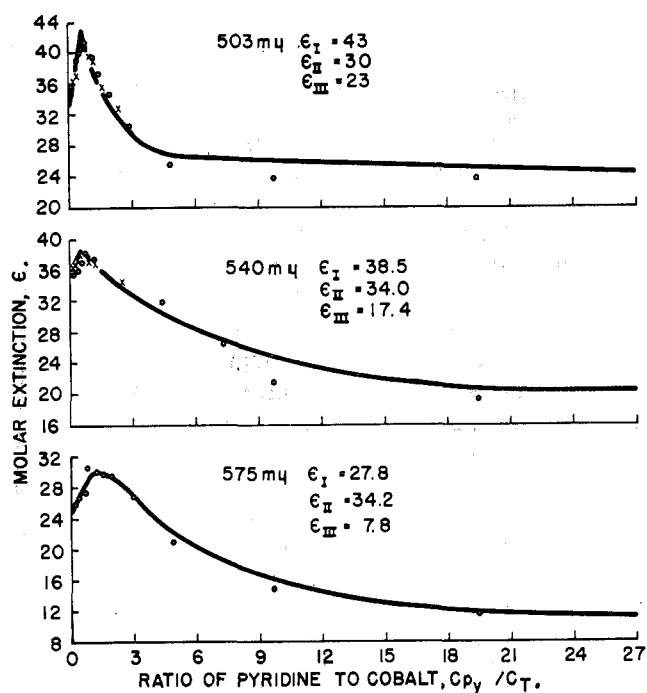
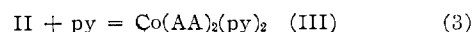
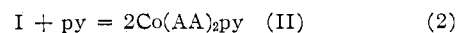
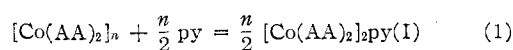


Fig. 2.—Observed molar-extinction at various ratios of pyridine to cobalt. Curves are calculated as described in body of paper. O indicates observed point with  $C_{\text{T}} = 4.84 \times 10^{-3} M$ , X represents observed point with  $C_{\text{T}} = 2.90 \times 10^{-3} M$ . Molar extinctions of various species at wave lengths concerned are indicated; a, 503  $m\mu$ ; b, 540  $m\mu$ ; c, 575  $m\mu$ .

the formation of a fairly stable species  $[\text{Co}(\text{AA})_2]_2\text{py}$ . The apparent linearity of the curves before  $C_{\text{py}}/C_{\text{T}} = 0.5$  and somewhat thereafter suggests that the equilibrium constant for the formation of this species is very large. The isolation of this species is presented in the Experimental section.

With the formation of  $[\text{Co}(\text{AA})_2]_2\text{py}$  essentially complete at  $C_{\text{py}}/C_{\text{T}} = 0.5$ , the spectra at larger ratios of pyridine to cobalt(II) can be analyzed assuming the presence of three species. It was impossible to explain the data without assuming a species with a cobalt to pyridine ratio intermediate to that of  $[\text{Co}(\text{AA})_2]_2\text{py}$  and the final species,  $\text{Co}(\text{AA})_2(\text{py})_2$ . The lack of clear breaks in the  $\epsilon_{\text{ob}}$  vs.  $C_{\text{py}}/C_{\text{T}}$  curves beyond  $C_{\text{py}}/C_{\text{T}} = 0.5$  indicates the formation of the intermediate species was not complete at any pyridine concentration used.

It was found that the following equilibria could be used to account for the data in a satisfactory manner.



At high  $C_{\text{py}}/C_{\text{T}}$  ratios, III is likely to be in equilibrium with only one additional cobalt(II) species. Assuming the concentration of I to be negligible beyond  $C_{\text{py}}/C_{\text{T}} = 10$ , a tentative value of  $K_3$  was obtained as follows. Since little change in absorbance from 575 to 650  $m\mu$  is observed at  $C_{\text{py}}/C_{\text{T}}$  ratios from 0.5–2.0 (Fig. 1, c,d,e), the molar extinction of I and the intermediate species II must be approximately the same in this spectral region. Estimates of  $\epsilon_{\text{I}}$  were made at  $C_{\text{py}}/C_{\text{T}} = 0.5$  and of  $\epsilon_{\text{III}}$  in 50% pyridine.<sup>11</sup> Assuming that  $\epsilon_{\text{I}} = \epsilon_{\text{III}}$  over the 575–650  $m\mu$  range, the ratio  $f_{\text{II}}/f_{\text{III}}$  was calculated.<sup>12</sup> From eq. 3 it can be shown that this ratio equals  $1/K_3 \cdot (\text{py})$ . A plot of  $f_{\text{II}}/f_{\text{III}}$  vs.  $1/C_{\text{py}}$  was found to be linear

(11) Extrapolated values of  $\epsilon_{\text{III}}$  agreed closely with values obtained in 50% pyridine solutions.

(12)  $f_{\text{II}}/f_{\text{III}} = (\epsilon_{\text{ob}} - \epsilon_{\text{III}})/(\epsilon_{\text{I}} - \epsilon_{\text{ob}})$ , assuming  $\epsilon_{\text{I}} = \epsilon_{\text{III}}$  and  $f_{\text{I}}$  negligible.

with  $C_{py}/C_T$  ratios greater than 10. This substantiated the validity of the assumptions made and suggested  $K_3$  to be  $\sim 50$  l. mole $^{-1}$ . The "free" pyridine concentration was estimated<sup>13</sup> over the range  $0.5 < C_{py}/C_T < 20$  by extrapolating the values obtained assuming  $f_I$  negligible ( $C_{py}/C_T > 10$ ). A value for  $f_{II}/f_{III}$  then was determined over the whole range of pyridine ratios. The point where  $f_{II} = f_{III}$  also was estimated.

Since the value of  $\epsilon_{ob}$  changed only slightly at some wave lengths with  $C_{py}/C_T > 5$  (see Table I), this suggested that  $f_I$  dropped rather rapidly from a value of 1 at  $C_{py}/C_T = 0.5$  to nearly zero near  $C_{py}/C_T = 5$ . A trial master curve was constructed similar to the final curve presented in Fig. 3. From this an estimate of  $K_2$  was obtained.

Using four experimental curves similar to those in Fig. 2, refinements were made in the values of  $f_I$ ,  $f_{II}$ , and  $f_{III}$  on the master curves until the experimental data were fitted. The value of  $\epsilon_I$  was determined as the extrapolated value of  $\epsilon_{ob}$  at  $C_{py}/C_T = 0.5$  and  $\epsilon_{III}$  was taken as the value of  $\epsilon_{ob}$  in 50% pyridine. At several wave lengths  $\epsilon_{II} \cong \epsilon_{III}$  as shown by the apparent isosbestic points at  $\sim 460$  and  $\sim 490$  m $\mu$ . The values of  $f_I$ ,  $f_{II}$ , and  $f_{III}$  were adjusted in accord with eq. 4.

$$\epsilon_{ob} = \epsilon_I f_I + \epsilon_{II} f_{II} + \epsilon_{III} f_{III} \quad (4)$$

The consistency of the equilibrium constants is seen in Table II. The accuracy of the final result was tested by the construction of  $\epsilon_{ob}$  vs.  $C_{py}/C_T$  curves at nine wave lengths. In these calculated curves, the value of  $\epsilon_{II}$  was determined at  $C_{py}/C_T = 3.0$  from the experimental data and the  $f_i$  values given in Table II.

TABLE II

CALCULATED EQUILIBRIUM CONSTANTS AND FRACTIONS OF SPECIES,  $C_T = 4.84 \times 10^{-3} M$

$C_{py}/C_T$	$f_I$	$f_{II}$	$f_{III}$	$f_{py}^a$	$K_2^b$	$K_3^b$
1	0.65	0.35	0	0.33	1.2	..
2	.33	.54	.13	1.04	1.7	48
3	.15	.60	.25	1.83	2.6	47
4	.085	.53 <sup>b</sup>	.38 <sup>b</sup>	2.66	2.5	56
5	.050	.47 <sup>b</sup>	.47 <sup>b</sup>	3.55	2.5	58
6	.040	.43	.53	4.49	2.1	57
7	.029	.39	.58	5.43	1.9	57
8	.017	.36	.62	6.39	2.4	56
9	.015	.33	.65	7.36	2.0	55
10	.014	.31	.67	8.31	1.6	54
11	.013	.29	.70	9.31	...	54
12	.011	.27	.72	10.3	...	54
13	.010	.25	.74	11.3	...	54
14	.009	.23	.76	12.3	...	55
15	.008	.22	.77	13.3	...	54
16	.006	.21	.78	14.2	...	54
17	.005	.20	.79	15.2	...	54
18	.004	.19	.81	16.2	...	54
19	.003	.18	.82	17.2	...	55
20	.002	.17	.83	18.2	...	55
Mean $\pm$ std. deviation					$2.0 \pm 0.4$	$54 \pm 3$

<sup>a</sup>  $f_{py} = (py/C_T) = C_{py}/C_T - (1/2f_I + f_{II} + 2f_{III})$ . <sup>b</sup>  $K_2 = f_{II}^2/f_I f_{py}$ ,  $K_3 = f_{III}/f_{II} f_{py} C_T$ .

This quantity along with the extrapolated values of

$$(13) (py) = C_{py} - (1/2f_I + f_{II} + 2f_{III})C_T.$$

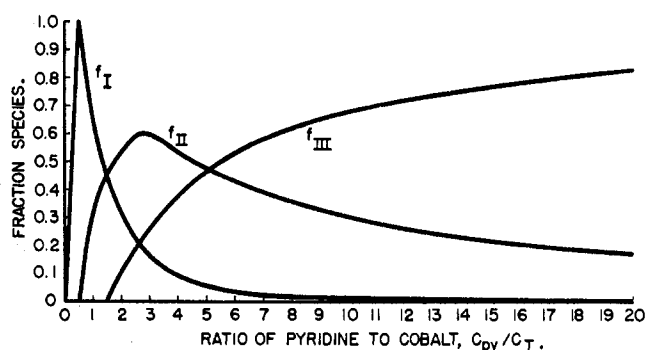


Fig. 3.—Master curve determined for fraction of species present at various ratios of pyridine to cobalt(II).

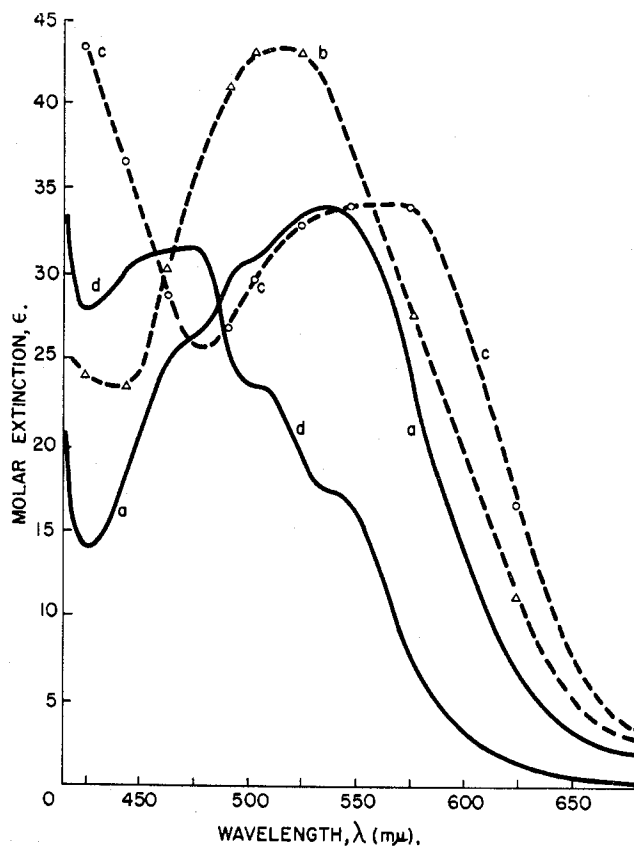


Fig. 4.—The visible spectrum of: a,  $\text{Co}(\text{AA})_2$ ,  $4.84 \times 10^{-3} M$ ; b,  $[\text{Co}(\text{AA})_2]_2\text{py}$ ; c,  $\text{Co}(\text{AA})_2\text{py}$ , and d,  $\text{Co}(\text{AA})_2(\text{py})_2$  in benzene; (b) and (c) were determined as described in body of paper.

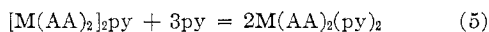
$\epsilon_I$  and  $\epsilon_{III}$ , when used with the  $f_i$  values, produced the calculated curves of Fig. 2. Similar curves at six additional wave lengths conformed equally well with the observed molar extinctions.

### Discussion

The reaction of  $\text{Co}(\text{AA})_2$  with pyridine in benzene has been shown to involve the formation of three species containing  $\text{Co}(\text{AA})_2$  and pyridine. Like the analogous reactions<sup>2</sup> with  $\text{Ni}(\text{AA})_2$  a polymeric species,  $[\text{Co}(\text{AA})_2]_2\text{py}$ , is found which has been isolated. This species may involve bridging acetylacetonate groups, similar to those found in  $[\text{Ni}(\text{AA})_2]_6$  and postulated for  $[\text{Ni}(\text{AA})_2]_2\text{py}$ , wherein the cobalt is surrounded in an "octahedral" fashion by the ligands. There is also

evidence that a 1:1 adduct of pyridine with  $\text{Co}(\text{AA})_2$  is formed in equilibrium with appreciable quantities of  $[\text{Co}(\text{AA})_2]_2\text{py}$  and/or  $\text{Co}(\text{AA})_2(\text{py})_2$ .

The formation of dipyridinate of  $\text{Co}(\text{AA})_2$  is shown not to be complete until very large excesses of pyridine are used, suggesting that  $\text{Co}(\text{AA})_2(\text{py})_2$  is considerably less stable than  $\text{Ni}(\text{AA})_2(\text{py})_2$ . This fact is further exemplified by comparing the formation constants for the dipyridinates of  $\text{Co}(\text{AA})_2$  and  $\text{Ni}(\text{AA})_2$  starting with the 2:1 species which appear to be formed completely. The equilibrium constant for reaction 5 in the case of nickel is  $2.7 \times 10^5 \text{ mole}^{-2} \text{ l.}^2$  while for  $\text{Co}(\text{AA})_2$



it is  $5.8 \times 10^3 \text{ mole}^{-2} \text{ l.}^2$ .

In Fig. 4 the visible spectra of  $\text{Co}(\text{AA})_2$  and  $\text{Co}(\text{AA})_2(\text{py})_2$  are compared with the spectra of  $[\text{Co}(\text{AA})_2]_2\text{py}$  and  $\text{Co}(\text{AA})_2\text{py}$  as determined at various wave lengths in this study. The similarity between the spectrum of  $\text{Co}(\text{AA})_2$  and the 2:1 adduct is particularly striking and would suggest that the coordination about the cobalt(II) is nearly the same in both cases.

The work of Cotton, *et al.*,<sup>14</sup> indicating intermolecular association of anhydrous  $\text{Co}(\text{AA})_2$  in benzene has been confirmed in this study. Cotton, *et al.*,<sup>14</sup> have shown that a temperature- and concentration-dependent association of  $\text{Co}(\text{AA})_2$  exists in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and

(14) F. A. Cotton, R. H. Soderberg, and J. A. Bertrand, to be published.

$\text{C}_6\text{H}_6$  using cryoscopic methods. They suggest that the molecular weight in  $\text{CCl}_4$  at  $77^\circ$  appears to indicate dimers ( $\pm 15\%$ ), while in freezing benzene values between that required for a trimer and that of a tetramer are obtained. Our results at  $37^\circ$  in benzene show that the average value of  $n$  ranges from 2.3 to 2.8 with concentrations ( $C_T$ ) between  $5 \times 10^{-3}$  and  $3.1 \times 10^{-2} M$ .

The spectrum deduced for the 1:1 addition product of  $\text{Co}(\text{AA})_2$  with pyridine, Fig. 4c, is almost identical with that of a 1:1 addition compound of cyclohexylamine with  $\text{Co}(\text{AA})_2$  which has been isolated by Cotton, *et al.*<sup>14</sup> An X-ray crystal structure of the latter product is being attempted.<sup>15</sup> The band systems observed in the 450–650  $m\mu$  region of the spectrum for the acetylacetonate complexes studied in this paper presumably are transitions from the  $^4T_{1g}$  ground state (in an octahedral field) to the  $^4T_{1g}(\text{P})$  level, split by reduction of symmetry and by spin-orbit coupling.<sup>16</sup> This assignment leads to a  $Dq$  value of about 950–1050  $\text{cm.}^{-1}$  for the acetylacetonate in these complexes, a value in agreement with that found previously in other acetylacetonate complexes.<sup>2</sup>

**Acknowledgment.**—This work was supported, in part, by the National Science Foundation.

(15) F. A. Cotton, private communication.

(16) C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill Book Co. Inc., New York, N. Y., 1962.

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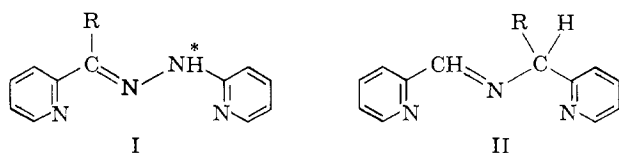
## Tridentate Chelate Compounds. III<sup>1</sup>

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A series of tridentate chelating agents has been prepared by condensing N-heterocyclic hydrazines of the amidrazone type, such as 2-pyridylhydrazine, with  $\alpha$ -acylated N-heterocycles, such as pyridine-2-aldehyde. These have been shown capable of coordinating with transition metal salts to give complex salts the cations of which can be de-protonated with alkalis to give intensely colored "neutral" complexes. Some of these are very stable. Some of their properties are discussed.

Coordination of the tridentate chelating agent 1,3-bis-(2'-pyridyl)-2,3-diaza-1-propene (I; R = H) with cobalt(II) salts has been shown<sup>3</sup> to lead to formation of diamagnetic cobalt(III) complex salts, the cations of which contain, coordinated with a cobalt atom, two residues of I (R = H) from one of which a proton has



(1) Previous paper in this series: H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 6415 (1959).

(2) Formerly Commonwealth Research Scholar; since 1962, Petroleum Research Fund Fellow, University of Sydney.

(3) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

been lost. We now report that bases can effect a similar deprotonation of the complex cations of salts derived by coordination of certain transition metal salts with bases of the series I (R = H or normal alkyl up to  $n$ -hexyl) or similarly constituted tridentate chelating agents prepared by interaction of a hydrazine derivative of a nitrogen heterocycle of amidrazone type with an acylated nitrogen heterocycle in which the carbonyl group is attached to a ring carbon atom adjacent to the nitrogen atom.

2-Pyridylhydrazine was condensed with 6-methylpyridine-2-aldehyde, quinoline-2-aldehyde, isoquinoline-1-aldehyde, isoquinoline-3-aldehyde, and, also, quinoline-8-aldehyde, in addition to a series of 2-acylpyridines  $\text{C}_5\text{H}_4\text{N}\cdot\text{CO}\cdot\text{R}$  (R =  $\text{CH}_3$  up to  $\text{C}_6\text{H}_{15}$ ). Pyridine-2-aldehyde also was condensed with 2-pyrimidi-