

## 868. Cobalt(II) Complexes of 2- and 4-Vinylpyridines

By N. H. AGNEW and L. F. LARKWORTHY

The cobalt(II) complexes  $\text{CoCl}_2(4\text{-vinylpyridine})_4$ ,  $\text{CoCl}_2(4\text{-vinylpyridine})_2$ , and  $\text{CoCl}_2(2\text{-vinylpyridine})_2$  have been isolated. Physical investigations have shown the first compound, which is pink, to be an octahedral monomer, and the other two compounds, which are intensely blue, to be tetrahedral monomers. No octahedral polymer of the type obtained with pyridine has been isolated. The failure to prepare an octahedral complex containing 2-vinylpyridine can be attributed to steric hindrance.

UNSTABLE blue and stable violet forms of the cobalt(II) compound  $\text{CoCl}_2(\text{pyridine})_2$  have long been known. X-Ray, magnetic, and spectroscopic investigations have shown the blue form to be a tetrahedral monomer, and the violet form a chloride-bridged octahedral polymer.<sup>1</sup> There have been recent thermodynamic<sup>2</sup> and thermal decomposition<sup>3</sup> studies of pyridine and substituted-pyridine complexes of cobalt(II). However, no 2-vinylpyridine (2-vpy), or 4-vinylpyridine (4-vpy), complexes have been reported. We have prepared the pink compound  $\text{CoCl}_2(4\text{-vpy})_4$ , and the deep blue compounds  $\text{CoCl}_2(4\text{-vpy})_2$  and  $\text{CoCl}_2(2\text{-vpy})_2$ . The formulæ and colours of these compounds indicate that the first is an octahedral monomer, and the others tetrahedral monomers. Such criteria alone can lead to wrong conclusions, but the structures have been confirmed by the physical investigations reported below.

*Magnetic Susceptibility Measurements.*—The results of magnetic susceptibility measurements from 90 to 300°K are given in Table I. The effective magnetic moments,  $\mu_{\text{eff}}$ , of the blue compounds are in the range 4.4—4.8 B.M., and independent of temperature, as expected for tetrahedral complexes, whereas  $\mu_{\text{eff}}$  for the pink compound, which is 4.97 B.M. at room temperature, varies considerably with temperature as expected for octahedral cobalt(II) complexes.<sup>4</sup>

*Conductance and Molecular-weight Measurements.*—All complexes were non-electrolytes in nitrobenzene. However, the pink  $\text{CoCl}_2(4\text{-vpy})_4$  gave a deep blue solution, and its spectrum was identical with that of  $\text{CoCl}_2(4\text{-vpy})_2$ ; two pyridine molecules are therefore completely dissociated.

TABLE I  
Variation with temperature of magnetic properties of cobalt(II)-vinylpyridine complexes

CoCl <sub>2</sub> (4-vpy) <sub>2</sub> , diamagnetic correction = $-180 \times 10^{-6}$ , $\theta = 2^\circ$								
$T(^{\circ}\text{K})$ .....	96.0	108.5	136.5	169.0	202.5	234.5	266.0	294.5
$10^4\chi_A$ .....	25,500	22,640	18,140	14,720	12,300	10,720	9437	8544
$\mu_{\text{eff}}$ (B.M.) .....	4.44	4.45	4.47	4.48	4.48	4.50	4.50	4.50
CoCl <sub>2</sub> (2-vpy) <sub>2</sub> , diamagnetic correction = $-180 \times 10^{-6}$ , $\theta = 6^\circ$								
$T(^{\circ}\text{K})$ .....	95.0	119.0	136.5	169.0	203.5	235.0	266.0	296.5
$10^4\chi_A$ .....	25,700	20,500	18,110	14,580	12,200	10,640	9345	8660
$\mu_{\text{eff}}$ (B.M.) .....	4.44	4.44	4.47	4.46	4.48	4.49	4.48	4.55
CoCl <sub>2</sub> (4-vpy) <sub>4</sub> , diamagnetic correction = $-300 \times 10^{-6}$								
$T(^{\circ}\text{K})$ .....	99.0	136.5	169.0	204.5	236.0	266.0	296.0	
$10^4\chi_A$ .....	27,150	20,770	17,240	14,720	12,800	11,410	10,340	
$\mu_{\text{eff}}$ .....	4.66	4.78	4.85	4.93	4.94	4.95	4.97	

The conductance results exclude dissociation of the chloride ion in the three compounds, and polymerisation isomers such as  $[\text{Co}(4\text{-vpy})_4][\text{CoCl}_4]$  for the blue compounds.

The results for the molecular weight of  $\text{CoCl}_2(4\text{-vpy})_2$  in acetone increased towards the

<sup>1</sup> N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.

<sup>2</sup> H. C. A. King, E. Körös, and S. M. Nelson, *J.*, 1963, 5449.

<sup>3</sup> J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1895.

<sup>4</sup> B. N. Figgis and R. S. Nyholm, *J.*, 1954, 12; 1959, 338.

theoretical value of 340 with concentration. Small amounts of a white solid, possibly a polymer, rapidly developed in acetone solutions of  $\text{CoCl}_2(2\text{-vpy})_2$ , so that accurate molecular-weight determinations were impossible, but this compound was much more dissociated than the 4-vinyl-substituted compound at similar concentrations.

Molecular-weight determinations showed the pink  $\text{CoCl}_2(4\text{-vpy})_4$  to be highly dissociated in methanol.

*Spectral Investigations.*—The visible spectra of the blue compounds in various solvents are given in Table 2. The family of peaks and the magnitudes of the extinction coefficients

Solvent and complex	Complex (M)	vpy added (M)	$\lambda_{\text{max.}}$ ( $m\mu$ ), $\epsilon$ in brackets
Nitrobenzene			
$\text{CoCl}_2(4\text{-vpy})_2$	0.00053	—	580(560), 613(800), ~636sh, ~660sh
$\text{CoCl}_2(2\text{-vpy})_2$	0.00098	—	609(270), 634(320), ~664sh
Ethanol			
$\text{CoCl}_2(2\text{-vpy})_2$	0.0030	—	585sh, ~620sh, 658(140)
	0.0031	0.012	585sh, ~620sh, 656(150)
	0.0030	0.036	585sh, ~620sh, 656(160)
	0.0031	0.73	581(230), 628(360), ~658sh
	0.0038	3.8	582(370), 621(550), ~634sh, ~660sh
	0.0030	100%	582(360), 618(520), ~636sh, ~658sh
	—	—	580, 615, ~625sh, ~655sh *
$\text{CoCl}_2(4\text{-vpy})_2$	0.0049	—	578(180), 612(260), ~627sh
	0.0058	0.012	578(270), 611(380), ~630sh, ~655sh
	0.0051	0.12	578(330), 611(470), ~632sh, ~655sh
	0.0051	0.83	577(130), 610(180), ~632sh, ~655sh
	0.0049	1.6	577(67), 610(84), ~632sh, ~655sh
	0.0050	4.8	510(28), 530(30), ~570sh, ~612(18), ~638sh
	0.0048	100%	503(33.5), 527(33), ~610sh, ~640sh
—	—	500, 530, ~610sh †	
Acetone			
$\text{CoCl}_2(4\text{-vpy})_2$	0.0059	—	578(540), 611(740), ~635sh, ~665sh
	0.0059	0.012	578(570), 611(800), ~635sh, ~665sh
	0.0060	0.086	578(550), 611(770), ~635sh, ~665sh
	0.0059	0.20	578(530), 610(730), ~635sh, ~665sh
	—	—	~590sh, 635, ~660sh *

\* Reflectance spectra. † Reflectance spectrum of pink  $\text{CoCl}_2(4\text{-vpy})_4$ .

are typical of tetrahedrally co-ordinated cobalt(II).<sup>1</sup> Except with  $\text{CoCl}_2(4\text{-vpy})_2$  in nitrobenzene, Beer's law was not obeyed, owing to dissociation of the substituted pyridine. Addition of 4-vinylpyridine to the blue ethanolic solutions of  $\text{CoCl}_2(4\text{-vpy})_2$  first increased the extinction coefficients, but in solutions more than 0.1M in vinylpyridine these decreased rapidly, the solutions becoming pink. The spectrum in 100% vinylpyridine was almost identical with the reflectance spectrum of  $\text{CoCl}_2(4\text{-vpy})_4$ . Thus, two additional substituted pyridine molecules are readily co-ordinated, but there is no marked formation of species such as  $[\text{Co}(4\text{-vpy})_6]^{2+}$ . There was no decrease in extinction coefficients with the 2-vinyl compound. Solutions in the amine itself, and ethanolic solutions containing much amine, gave almost identical spectra, so it is unlikely that more than two 2-vinylpyridine molecules can co-ordinate to the metal.

In acetone, a ten-fold increase in concentration from 0.001M increased the extinction coefficients for  $\text{CoCl}_2(4\text{-vpy})_2$  by 10% only. The effect of the addition of 4-vinylpyridine on the extinction coefficients also indicated that the compound was only slightly dissociated in acetone, which is in agreement with the molecular-weight measurements.

The reflectance spectra of the blue compounds were less well resolved than, but very similar to, the solution spectra obtained from solutions of maximum extinction coefficient. This confirms the tetrahedral structure for the solids deduced from the magnetic data.

2-Vinylpyridine has been reported to form the copper chelate,  $\text{CuCl}_2(2\text{-vpy})$ .<sup>5</sup> However, only qualitative information was presented for co-ordination of the vinyl group, and

<sup>5</sup> J. F. Pudvin and J. A. Mattern, *J. Amer. Chem. Soc.*, 1956, **78**, 2104.

the analytical results were poor. Chelation of 2-vpy is unlikely, because of the relative disposition of the nitrogen and vinyl group donor-electron pairs. As expected, no evidence has been found for the co-ordination of the vinyl group. The visible spectra resemble those of the cobalt-pyridine complexes, and the weak vinyl group stretching absorptions near  $1635\text{ cm}^{-1}$  in the infrared spectra of the vinylpyridines are almost unaltered in the complexes. These absorptions are absent in metal-containing polymers of the vinylpyridines.

The failure to prepare an octahedral cobalt(II) compound, either monomeric or polymeric, containing 2-vinylpyridine is probably due to steric hindrance by the vinyl substituents. Recent work has shown 2-methyl groups to act in this way.<sup>2</sup>

#### EXPERIMENTAL

*Purification of Vinylpyridines.*—2-Vinylpyridine (B.D.H.) was dried over potassium hydroxide pellets for 24 hr., and then distilled under nitrogen. The fraction, b. p.  $54-54.5^\circ/15\text{ mm.}$ ,  $n_D^{25} = 1.5462$ , was taken. Gas-liquid chromatography with a column of 10% Carbowax-1000 on Celite 125 showed the material to be pure.

4-Vinylpyridine (Light and Co.) was purified as above. Two fractionations were necessary to reduce the impurities, as shown by gas chromatography, to less than 1%. The fraction, b. p.  $64.8^\circ/15\text{ mm.}$ ,  $n_D^{25} = 1.5480$ , was taken. Two, and possibly three, impurities were present, but a comparison of the retention times with that of 2-vinylpyridine showed that the impurities did not include this amine.

*Dichlorodi-(4-vinylpyridine)cobalt(II).*—To a solution of cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (2.4 g., 0.01 mole), in redistilled ethanol (10 ml.) was added with stirring a solution of 4-vinylpyridine (2.1 g., 0.02M) in ethanol (5 ml.). After 1 hr. the blue, crystalline complex was filtered off, washed with ether containing a few drops of amine, and dried for 1 hr. at 15 mm.; the yield was 2.6 g. The molecular weight was 270 in 0.01M-solution in acetone and 330 in 0.04M-solution (theory, 340) (Found: C, 49.5; H, 4.5; N, 8.1; Co, 17.3.  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Co}$  requires C, 49.4; H, 4.2; N, 8.2; Co, 17.3%).

*Dichlorotetra-(4-vinylpyridine)cobalt(II).*—The pink complex was prepared by adding cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (4.8 g., 0.02 mole), in ethanol (20 ml.) to 4-vinylpyridine (8.4 g., 0.08 mole) in ethanol (15 ml.). More 4-vinylpyridine (3 g.) was then added, and pink crystals (10.4 g.) separated after a few minutes from the magenta solution. The product was washed with ether containing a few drops of 4-vinylpyridine, and dried for 1 hr. at 15 mm. (Found: C, 61.0; H, 5.0; N, 10.1; Co, 10.8.  $\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Co}$  requires C, 61.1; H, 5.1; N, 10.2; Co, 10.7%).

Recrystallisation from ethanol gave the blue complex. In all the organic solvents tried, except methanol, the pink compound gave blue solutions. Methanol gave pink solutions with this complex, and with the blue tetrahedral complex, and apparently decomposed both. The compound turned blue in contact with non-solvents such as ether and toluene.

*Dichlorodi-(2-vinylpyridine)cobalt(II).*—This blue, crystalline compound was prepared similarly to the corresponding 4-vinylpyridine compound (Found: C, 49.2; H, 4.3; N, 8.2; Co, 17.4.  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Co}$  requires C, 49.4; H, 4.2; N, 8.2; Co, 17.3%). In methanol it gave a pink solution. It gave blue solutions with polar organic solvents, but in acetone and chloroform insoluble material, perhaps a polymer, rapidly developed.

*Physical Measurements.*—The magnetic measurements were carried out by the Gouy method with the apparatus already described.<sup>6</sup> Conductance measurements were made with a Philips bridge type GM4249. Visible spectra in solution were recorded on a Perkin-Elmer 137 recording spectrophotometer. Reflectance spectra were recorded with a Unicam S.P. 500 spectrophotometer fitted with a diffuse reflectance attachment, the blue compounds being diluted with lithium fluoride. Molecular weights were determined with a Mechrolab vapour pressure osmometer, model 201A.

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CHEMISTRY DEPARTMENT, BATTERSEA COLLEGE OF TECHNOLOGY, LONDON S.W.11.

[Present address (N. H. A.): N.C.R.L., C.S.I.R.,  
P.O. Box 395, PRETORIA.]

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<sup>6</sup> A. Earnshaw, *Lab. Practice*, 1961, **10**, 294.