to the dehydration and added from time to time during isolation of the product.

Dehydration at Reduced Temperature and Pressure.—A mixture of 40 g. of the alcohol, 81 mg. of iodine and 0.4 g. of 2,5-dihydroxy-1,4-benzoquinone was heated for 125 minutes at a bath temperature of 168–186° and aside from occasional fluctuations the product was collected in the range 79–95.5°. The system was maintained at 454–494 mm. during this period, except for about 20 minutes when it was lowered to 401–408 mm. The distillate and the undistilled residue were treated separately and yielded 6.6 g. of styrene, b. p. 49.5–50.8° (28 mm.); $n^{22}D$ 1.5449 (lit.[13] 1.5460). Fractionation of the remaining material gave an additional 0.2 g. of styrene, b. p. 53–63° (32 mm.) (total yield 20%), 3.2 g. of reddish-golden colored (impure) phenylmethylcarbinol, b. p. 106–113° (29.5–31 mm.); m. p. of α-naphthylurethan[16] 105.8° (mixed m. p. with an authentic sample not depressed), and 11.2 g. (30.3%) of α,α'-diphenyldiethyl ether, b. p. 165–170° (28–28.5 mm.). The purified ether was a colorless oil with a very faint pleasant odor, b. p. 169.7–170.7° (31 mm.) (lit.[17] 175–177 (31 mm.)); $n^{25.5}D$ 1.5391; $d^{25.5}_4$ 1.000 (lit.[9] d^{15}_4 1.0058).

Anal.[18] Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.76, 84.91; H, 7.99, 8.06.

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The Magnetic Susceptibility of Vitamin B_{12}

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It is naturally of interest to determine the valence of the cobalt atom present in the vitamin B_{12} molecule. The behavior of the material in a magnetic field offers one way to do this. Although the simple salts of bivalent and trivalent cobalt are paramagnetic (three and four unpaired electrons, respectively), the situation is quite different among the coördination compounds. With the exceptions to be noted, the cobaltous ammines are paramagnetic, the cobaltic diamagnetic. The magnetic moments of the cobaltous ammines (these are taken to include the chelate ring compounds) fall between 1.73 and 5.50[1,2] Bohr magnetons, depending on whether the bonds are essentially covalent or ionic. The exception to this is a limited number of cobaltous compounds which have the property of reversibly absorbing and releasing molecular oxygen; the deoxygenated forms of such materials are paramagnetic, the oxygenated forms diamagnetic. The first of these materials, bi-(disalicylalethylenediimine)-μ-aquo-dicobalt, was discovered by Pfeiffer and Tsumaki[3,4] and investigated later in detail by Diehl[5] and others. Michaelis[6] later showed that a solution of cobaltous chloride, ammonia and ammonium chloride possessed these same properties. The cobalt histidine compound investigated by Burk and his co-workers[7] was shown by Michaelis[8] to become diamagnetic on oxygenation.

Although practically all of the numerous hexacovalent cobaltic compounds are diamagnetic[9] there are a few exceptions. Potassium hexafluocobaltate, $K_3[CoF_6]$, is paramagnetic from which it is inferred that the cobalt–fluoride bonds are essentially ionic. The few binuclear cobaltic ammines containing peroxo-, bridging groups which have been examined have been reported contradictorily as being diamagnetic[10,6] and paramagnetic[11,12]; it has been assumed that these compounds contain both tri- and quadrivalent cobalt. This is a subject which needs re-examination.

In view of the sharp difference in the magnetic moment between the coördination compounds of the two valence states, it seems likely that the magnetic behavior of vitamin B_{12} should afford some clue to the valence of the cobalt in the molecule.

Experimental Work

Apparatus.—The measurements were made by the Gouy method using a magnet built by the Consolidated Engineering Company of Pasadena, Calif., their Model 23-104A. This magnet developed a field of 11,000 gauss at 10 amp. Power was supplied to the magnet by a dry plate rectifier preceded by a voltage regulator of large capacity. The power supply was provided with a reversing switch so that following a series of measurements at progressively increasing field strengths, a reverse current could be passed of sufficient size to remove the residual field. A semi-micro balance, Ainsworth Type TCX, was used. Two tubes of the usual type with a glass septum at the center were used, tube A having an internal diameter of 0.24 cm. and B an internal diameter of 0.46 cm. The material was placed in the upper part of the tube, the column of material extending well out of the field. No particular provision was made for temperature control other than to maintain the room temperature about 25°; at 10 amp. the magnet did not heat sufficiently to raise the temperature appreciably during a measurement.

Material.—Crystalline vitamin B_{12}, 1.2 g., was supplied by E. R. Squibb and Sons of New Brunswick, N. J. This material was used without further purification.

Procedure.—Solid materials were well packed into the tubes by tapping the tube one hundred times after each small addition of material. Sufficient time, upwards of

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[5] Diehl, *et al.*, *Iowa State Coll. J. Sci.*, **21**, 271, 278, 287, 311, 316, 326, 335 (1947); **22**, 91, 110, 126, 129, 141, 150, 165 (1948); **23**, 273 (1949).

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[7] Burk, Hearon, *et al.*, *J. Biol. Chem.*, **165**, 723 (1946); *Fed. Proc.*, **6**, 242, 259, 260 (1947); **7**, 148 (1948); *J. Nat. Cancer Inst.*, **9**, (1948).

[8] Michaelis, *Arch. Biochem.*, **14**, 17 (1947).

[9] Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).

[10] Feytis and Haller, *Compt. rend.*, **152**, 708 (1911).

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an hour, was allowed for thermal equilibrium to be established between the tube and the surrounding glass jacket and magnet, otherwise drift in weight of a few hundredths of a milligram occurred during the measurement. Measments were made usually with currents of 6.00, 8.00 and 10.0 amp. In some of the later measurements where the presence of ferromagnetic impurities was suspected measurements were made at 1.00-amp. intervals Following a series of measurements, a small reverse current was passed through the magnet to remove the residual field and a check made on the initial weight of the tube

Measurements with Tube A.—The tube was calibrated with water and with ferrous ammonium sulfate. The density reported is the effective or bed density. Two measurements were made on vitamin B_{12}, the tube being repacked for the second measurement.

Change in weight of material, mg.

Current, amp.	Water (wt. 0.6920 g., *d* 1.00)	B_{12} (0.4570 g., *d* 0.660)	B_{12} (0.754 g., *d* 0.688)	Ferrous ammonium sulfate (0.7119 g., *d* 103)
1	−0.51		+0.05	+ 2.73
2	− .44		+ .20	+10.61
3	− .65		+ .31	
4	− .95		+ .36	+35.96
5	−1.16		+ .37	
6	−1.51	+0.57	+ .37	+56.33
7	....		+ .37	
8	−1.76	+0.55	+ .36	+71.18
9	−1.85		+ .36	
10	−1.90	+0.53	+ .35	+83.06

The observed changes in weight of water and of ferrous ammonium sulfate were more or less linear with the changing current. On the other hand only a small increase in weight (paramagnetic effect) was found for B_{12} for currents up to 6 amp. and at higher currents no increase at all; such behavior is characteristic of a diamagnetic material containing a ferromagnetic impurity. Even by taking the maximum increase in weight of B_{12}, the paramagnetic susceptibility calculates out (on the second measurement) to be a very small value: $\chi = +0.247 \times 10^{-6}$ using water as reference ($\chi = -0.720 \times 10^{-6}$), and corrected for the effect of air in the lower part of tube using $k = +0.029 \times 10^{-6}$, and $+0.246 \times 10^{-6}$ using ferrous ammonium sulfate as reference ($\chi = +31.7 \times 10^{-6}$). Assuming the molecular weight of B_{12} to be 1500, this gives a molar susceptibility of $+370 \times 10^{-6}$ and a magnetic moment of 1.18; the latter value is far below the moment expected for one unpaired electron ($\mu = 1.73$). It is therefore apparent that B_{12} is diamagnetic.

Measurements with Tube B.—The tube was calibrated with water and as a check a measurement was made on bi-(disalicylalethylenediimine)-μ-aquo-dicobalt, the molar susceptibility of which has been reported[5] as $\chi_M = +3160 \times 10^{-6}$.

Change in weight of material, mg.

Current, amp.	Water (Wt. 1.701 g., *d* 1.00)	B_{12} (1.191 g., *d* 0.700)	Bi-(disalicylal-ethylene-diimine)-μ-aquo-dicobalt (0.7429 g., *d* 0.437)
1	−0.20	+0.49	+ 1.89
2	−0.79	+1.23	+ 7.37
3	−1.84	+1.82	+15.64
4	−3.01	+2.19	+25.34
5	−3.98	+2.37	+34.59
6	−4.81	+2.49	+40.04
7	−5.53	+2.49	+45.86
8	−6.15	+2.49	+51.82
9	−6.70	+2.49	+55.28
10	−7.21	+2.49	+59.36

As in tube A vitamin B_{12} exhibited a very small paramagnetic effect varying with the field strength ($\chi = +0.415 \times 10^{-6}$, $\chi_M = +623 \times 10^{-6}$ and $\mu = 1.22$ using the maximum change in weight and reference at 10 amp. and water as reference, and $\chi = +0.283 \times 10^{-6}$, $\chi_M = 424 \times 10^{-6}$ and $\mu = 1.01$, using the cobalt compound as reference). It is therefore necessary to conclude again that vitamin B_{12} is diamagnetic.

Discussion

Since vitamin B_{12} is diamagnetic, it becomes pertinent to ask if the cobalt atom of the molecule may not actually be paramagnetic and its paramagnetism covered by the diamagnetism of the large organic molecule. In the absence of the cobalt-free organic component for direct measure, the diamagnetic moment can only be calculated. Using Pascal's constants[13] and the formula proposed by Brink and co-workers,[14] $C_{62}H_{86-90}N_{14}O_{13}PCo$, gives a value for χ_M of about -780×10^{-6}, the uncertainty amounting to probably $\pm 75 \times 10^{-6}$, owing to the lack of knowledge of the nature of the binding of the oxygen and nitrogen atoms and of the constitutive factors. The minimum magnetic moment for the cobalt atom would correspond to one unpaired electron, $\mu = 1.73$ or at room temperature $\chi_M = 1300 \times 10^{-6}$. The calculated diamagnetic moment would be far short of concealing a paramagetic moment were it present.

The ferromagnetic impurity apparently present in the crystalline vitamin B_{12} used probably does not exceed a few thousandths of one per cent. It will be interesting to repeat the measurement sometime after a recrystallization technique has been worked out which will eliminate the trace of iron or iron oxide probably present.

Inasmuch as it now appears that vitamin B_{12} is diamagnetic and in view of the magnetic character of the coördination compounds of cobalt in its two valence states as reviewed above, it may be concluded that the cobalt is present in the molecule in the trivalent state or in the bivalent state coupled with molecular oxygen.

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DEPARTMENT OF CHEMISTRY
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The Isolation of Menthofuran from American Peppermint Oil

BY RICHARD H. EASTMAN

Menthofuran (I) a terpenoid substance of unusual structure has been isolated from peppermint