Technical Papers

The Magnetic Susceptibility of Vitamin B_{12} and B_{12b}

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It has been stated by Rickes, Brink, Konivszy, Wood, and Folkers (*1*) that vitamin B_{12} probably is a hexacoordinated cobalt complex, although these authors do not cite the experimental evidence on which this conclusion is based.

Magnetic measurements on pure samples of vitamin B_{12} and related cobalt compounds may be expected to yield unambiguous evidence concerning the nature of the bonding of the cobalt moiety of these substances. We have available an apparatus for measuring the magnetic susceptibilities of very small samples of solid compounds (*2*). Through the courtesy of various pharmaceutical laboratories, we have been supplied with samples of vitamin B_{12} and B_{12b} in quantities sufficient for magnetic measurements.

The susceptibilities were measured by a modification of the Faraday method, using a sensitive quartz fiber torsion balance to measure the magnetic forces and a 5-in. alnico permanent magnet, with pole pieces especially cut to provide a small region of uniform dH/dx. Since neither the field strength nor its rate of change in the experimental region was known accurately, our measurements are comparative and refer in all cases to the behavior of the test samples as compared with that of samples of reagent grade $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ under the same experimental conditions. In computing our results, we have taken the value of χ for our reference standard to be 29.45×10^{-6} cgs units. All measurements were made at room temperature and in air. No corrections were made for the influence of the slight susceptibility of the surrounding air, since these corrections were, in general, of a smaller order of magnitude than the experimental error of the measurements themselves.

In all cases in which the quantity of sample was sufficient, at least two portions of the same preparation were investigated separately. This served as a test both for magnetic homogeneity of a particular preparation and to reveal any significant contamination with magnetically active material resulting from our own handling of a sample in preparation for a run.

The results of our measurements are summarized in Table 1.

TABLE 1

MAGNETIC SUSCEPTIBILITIES OF VARIOUS SAMPLES OF VITAMIN B_{12} AND B_{12b}

Compound	Source	Run No.	Sample Wt (mg)	χ (cgs × 10^6)	χ_m Mol Wt = 1490 (*3*)	u_{eff} (Bohr Magnetons)	Remarks
B_{12}	A	1	0.41	− 0.69			
B_{12}	A	2	.50	− 0.69			
B_{12}	B	1	.15	Diamagnetic (−)			Sample too small for accurate measurement
B_{12}	C	1	.25	− 0.63			
B_{12}	C	2	.15	Diamagnetic (−)			Sample too small for accurate measurement
B_{12}	D	1–3		Variable paramagnetism (+)			Samples inhomogeneous
B_{12}	E	1	.72	+ 5.88	+ 8760	4.45	
B_{12}	E	2	.40	+ 5.83	+ 8690	4.45	
B_{12}	E	3	.40	+ 5.40	+ 8050	4.36	
B_{12}	F	1	.40	− 1.17			
	F	2	.39	+ 1.01			
B_{12b}	G	1	.47	− 0.70			
B_{12b}	G	2	.57	− 0.54			
B_{12b}	H	1	0.33	+ 0.30			
B_{12b}	I	1–2		Variable paramagnetism (+)			Samples inhomogeneous

A. The Upjohn Company, Research Laboratories, Kalamazoo, Mich., Vitamin B_{12}, No. 223-WGJ-6.
B. *Idem.*, No. 249-WGJ-7 (Merck lot #9R-6537).
C. *Idem.*, No. 247-WGJ-7.
D. British Drug Houses, Ltd., London, Eng.
E. Merck & Co., Inc., Rahway, N. J., Vitamin B_{12}, No. 9R-5,168.
F. Lederle Laboratories Division, Pearl River, N. Y., Vitamin B_{12}, No. NP-86-8-1.
G. The Upjohn Company, Research Laboratories, Vitamin B_{12b}, No. 233-WGJ-7.
H. *Idem.*, No. 239-WGJ-7.
I. Lederle Laboratories Division, Vitamin B_{12b}, No. NP-92-184-7.

Of the 6 preparations of vitamin B_{12} examined by us, 3 (Upjohn samples 223-WGJ-6, 249-WGJ-7, and 247-WGJ-7) were clearly diamagnetic and are unquestionably covalent cobaltic complexes with octahedral d^2sp^3 bonding.

The Lederle sample (NP-86-8-1) exhibited both diamagnetic and paramagnetic behavior. Since the sample appeared homogeneous we conclude that the paramagnetism is due to some slight impurity and that the pure B_{12} is a covalent cobaltic complex.

Two preparations (British Drug House and Merck 9R-5168) showed paramagnetic behavior. The British Drug Houses preparation as received by us in a sealed glass tube was visibly inhomogeneous; it was evident that a part of the sample had been charred in sealing the tube. Since charring would be expected to produce a mixture of carbon and strongly paramagnetic cobaltous phosphate, we attach no significance to either the sign or magnitude of the susceptibility of this preparation.

The Merck preparation appeared to be homogeneous and gave consistent results on repeated measurement. The Bohr magneton number of this material, calculated from the susceptibility after correcting for the diamagnetic contribution of the remainder of the molecule, is in fairly good agreement with that expected for an ionic compound of Co^{II}. However, the variable orbital contribution found in different cobaltous compounds somewhat diminishes the significance of the exact magnitude of the magneton number.

In spite of the agreement between different runs on this material and the fact that the susceptibility is quite consistent with that expected for an ionic Co^{II} compound, we are inclined to suspect that this result is due to uniform contamination with a small amount of strongly paramagnetic or ferromagnetic impurity. Since we are not equipped to measure the field strength dependence of the susceptibility, the last-mentioned possibility could not be investigated experimentally. The question as to whether vitamin B_{12} may exist in one form as cobaltous compound undoubtedly justifies further laboratory investigation.

We regard it as significant that the Merck 9R-5168 sample was not obviously different in color or appearance from other samples of B_{12} which were diamagnetic.

Of 3 samples of vitamin B_{12b}, one (Upjohn 233-WGJ-7) was diamagnetic, and consequently must be a hexacoordinated covalent cobaltic complex. Another sample (Upjohn 239-WGJ-7) was available in smaller amount, but one run showed it to exhibit weak paramagnetism. We believe this result probably is due to the presence of a para- or ferromagnetic impurity. The third (Lederle NP-92-184-7) had been charred in sealing the tube, and the erratic paramagnetism is without significance.

In summary, samples of vitamin B_{12} and vitamin B_{12b} have been found to exist in the form of covalent cobaltic complexes with octahedral d^2sp^3 bonding. The possibility that these substances may exist as cobalt compounds exhibiting other types of bonding requires further investigation.

References

1. Rickes, E. L., *et al. Science*, **108**, 134 (1948).
2. Cunningham, B. B. *Nucleonics*, **5**, 62 (1949).
3. Brink, N. G., *et al. J. Am. Chem. Soc.*, **71**, 1854 (1948).

Some Adsorption Colors and their Significance for Tautomeric and Thermochromic Effects

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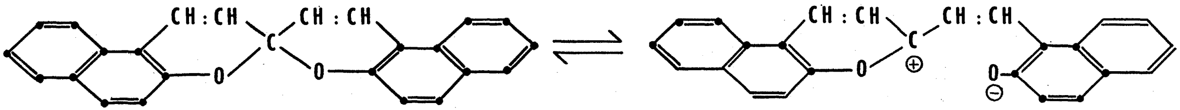
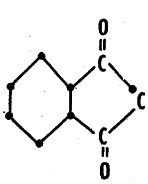
Some spiropyrans are colorless substances which form colorless solutions in cold inert solvents, whereas the hot solutions are intensely colored, e.g., violet-blue in the case of β-dinaphthaspiropyran (I); the phenomenon is reversible. The color change is usually explained by the formation of a heteropolar molecule, betaine (*1*), (compound II).



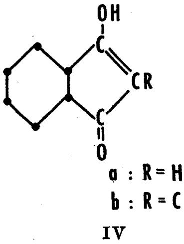
I

II

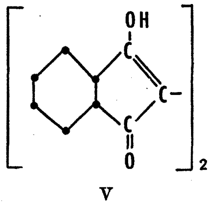
The correctness of this hypothesis was recently questioned by Hukins and Le Fèvre (*2*), but the proof of the explanation outlined here may be seen from the following experiment. When a piece of activated alumina[1] is added to the cold colorless solution of (I) in xylene, the surface of the colorless alumina becomes bluish-green immediately. Using a column of activated alumina, the adsorbed material may be eluted by means of methyl alcohol. This experiment is reminiscent of the observations by Weitz and coworkers (*3*). It was found that the colorless triarylmethyl halides and related substances were adsorbed with the color of the corresponding cation or a similar color, e.g., the colorless triphenylmethyl chloride gives the yellow color of the triphenylmethyl cation, and the colorless base $[(CH_3)_2N \cdot C_6H_4]_3C \cdot OH$ is adsorbed with the violet color of the corresponding cation.



III



IV



V

In benzene, 1,3-diketohydrindene (III) gives a colorless solution. When a piece of activated alumina is added to a cold solution of (III) in benzene a violet color results at once. It seems that the violet color is due to the enol form (IVa). Compound IVb is dark red (*4*), and V is violet (*5*).

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[1] Obtained from Peter Spence and Sons, Ltd., London.