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COBALT (I) MESO-TETRAPHENYLPORPHYRIN

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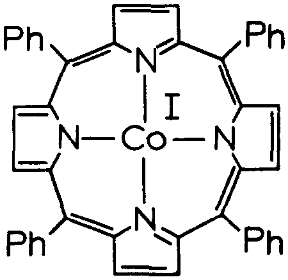
The peculiar chemical and biological properties of vitamin B_{12} and its derivatives (3) have made chemical investigations of planar cobalt (I) complexes of considerable interest. We wish to report here the preparation and characterization of cobalt (I) meso-tetraphenylporphyrin (I).



I

Cobalt (II) meso-tetraphenylporphyrin (II) is readily reduced by the following reagents (4): sodium amalgam in pyridine or tetrahydrofuran, sodium borohydride in ethanol, acetonitrile or pyridine, and pyridine borane in pyridine. A single air sensitive product, $\lambda_{max}^{pyridine}$ 608 mu (2.2×10^3), 511 mu (1.5×10^4), 427 mu (6.6×10^4), 362 mu (5.4×10^4), is formed by the different reducing agents as evinced by the visible spectra of the various reaction products. The sodium borohydride-pyridine and pyridine borane reductions are quite slow at room temperature but are markedly accelerated by visible light. Isobestic points (at 430, 547, 597 and 620 mu in the sodium borohydride-pyridine reduction) can be observed. Hantzch's ester, ascorbic acid, 1,3-propanedithiol, thioglycolic acid and sodium dithionite in pyridine lead to no reduction of II, either thermally or photochemically.

The formation of diamagnetic cobalt (I) species by reduction of vitamin B_{12} (5,6) and cobalt phthalocyanines (7,8,9,10) is now well established. We formulate the reduction product of cobalt (II) meso-tetraphenylporphyrin as the spin-paired cobalt (I) porphyrin I on the basis of the following experiments:

1) Reduction of II using one or more gram-equivalents of sodium amalgam in pyridine leads to the complete production of I; use of less than one equivalent of sodium amalgam leads to a proportionately smaller extent of

reduction. Opening solutions of I in pyridine or tetrahydrofuran to air leads to the immediate production of a mixture of cobalt (II) and (III) porphyrin, thereby excluding the possibility that reduction of the porphyrin ring had occurred. The reduction product quantitatively reacts with cobalt (II) phthalocycanine in pyridine, the products being the cobalt (II) porphyrin and cobalt (I) phthalocyanine. Porphyrin I is accordingly a one-electron reduction product of II.

2) As a 0.07 molar solution in tetrahydrofuran the NMR spectrum of I can be observed. The porphyrin ring hydrogens appear as a singlet at δ 8.28(2H) and the phenyl hydrogens appear as two multiplets centered at δ 8.10(2H) and δ 7.67(3H), relative to internal (and external) tetramethylsilane. Opening the sample to air leads to immediate disappearance of the porphyrin spectrum, broadening of the solvent peaks, and appearance of two signals for the internal and external tetramethylsilane ($\Delta\nu$ = 15.5 cps) (11). Gouy balance experiments indicate that, as a 0.05 molar solution in tetrahydrofuran, I is diamagnetic, having $X_M = -306 \pm 150 \times 10^{-6}$ (12).

3) Like other cobalt(I) species (13,14), I is capable of catalyzing the sodium borohydride reduction of nitrobenzene. In this case, however, not aniline but phenylhydroxylamine (34% yield) and azoxybenzene (35% yield)

are the major products. Ion pair formation and/or specific solvation effects are unimportant spectrally, if present at all, since the spectrum of I is insensitive to method of formation (15) or a thousand-fold change in concentration. The methods of preparation, in particular sodium amalgam in tetrahydrofuran, require that I not be a hydrido cobalt porphyrin. The conjugate acid (hydrido cobalt) of I is unstable; addition of adipic acid to a tetrahydrofuran solution of I quickly regenerates II.

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REFERENCES

1. Alfred P. Sloan Research Fellow.
2. National Institutes of Health Predoctoral Fellow.
3. Conference on Vitamin B_{12} Coenzyme, Ann. New York Acad. Sci., 112, 547 (1964).
4. All manipulations were carried out in a standard vacuum line, using break-seals for addition of reagents.
5. J. W. Collat and J. C. Abbott, J. Am. Chem. Soc., 86, 2308 (1964).
6. H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, Chemistry and Industry, 197 (1904).
7. Cobalt (I) phthalocyanines were first reported but not explicitly recognized as such in the patent literature, quoted by F. H. Moser and A. L. Thomas in "Phthalocyanine Compounds", Reinhold Pub. Corp., New York,

1963, pp. 257-64.

8. R. Taube, M. Zach, K. A. Stauske, and S. Heidrich, Zeit. Chem., 3, 392 (1963).

9. D. H. Busch, J. H. Weber, D. H. Williams and N. J. Rose, J. Am. Chem. Soc., 86, 5161 (1964).

10. See also G. N. Schrauzer and J. Kohnle, Chem. Ber., 97, 3056 (1964).

11. D. F. Evans, J. Chem. Soc., 2003 (1959).

12. Magnetic susceptibility measurements were determined at 4.4, 5.4 and 6.2 kgauss. The text value was derived in the standard manner (P. W. Selwood, "Magnetochemistry", Interscience, 1956) and is for the complex, not the cobalt. The porphyrin ligand has a molar susceptibility (X_M) of $-434 \pm 4 \times 10^{-6}$ (calcd., -363×10^{-6}).

13. A. A. Vlcek and A. Rusina, Proc. Chem. Soc., 161 (1961).

14. R. D. Gillard and G. Wilkinson, J. Chem. Soc., 3594 (1963).

15. Sodium borohydride and pyridine borane as reducing agents give the same result spectrally.