

[CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

The Existence of Spin-Paired Cobalt(I) in a Reduced Form of Cobalt 4,4',4'',4'''-Tetrasulfophthalocyanine

BY DARYLE H. BUSCH, JAMES H. WEBER, DONALD H. WILLIAMS, AND NORMAN J. ROSE

RECEIVED OCTOBER 12, 1964

The anion of cobalt tetrasulfophthalocyanine is reduced by a variety of materials to a diamagnetic species that is most reasonably considered to be a derivative of the spin-paired cobalt(I) ion. P.m.r. measurements show that the alternate formulation as a hydride of cobalt(III) is wrong. These results are used to infer that the probable state of the cobalt atom in the so-called hydridocobalamin is also not a hydride of cobalt(III), but a derivative of the highly nucleophilic cobalt(I) ion.

Introduction

Considerable interest has been shown in recent years concerning the lower oxidation states exhibited by cobalt in complicated chelate compounds.¹⁻⁴ This is particularly true of those containing cobalt in square-planar or five-coordinate structures. We have observed the chemically reversible reduction of cobalt(II) tetrasulfophthalocyanine at room temperature in aqueous solution to a species that is most simply characterized as a derivative of spin-paired cobalt(I). This result is particularly significant in view of the difficulties that have attended the establishing of the relationships relating to the oxidation states and electronic structures of the cobalt atom in the reduced derivatives of vitamin B₁₂.⁵⁻⁸ Although the symmetries of the principal ligands in B₁₂ and tetrasulfophthalocyanine are distinctly different, it is to be expected that the four strong "in-plane" donor atoms will have somewhat similar effects on the electronic structures and thermodynamic properties of the central atom. Consequently, the species reported here provides a useful model relevant to the formulation suggested for the so-called hydridocobalamin⁹ and vitamin B₁₂ coenzyme.

Results and Discussion

Magnetic studies on aqueous solutions of cobalt(II) tetrasulfophthalocyanine have provided the most direct evidence for the existence of the reduced species (Table I). The action of either sulfide ion or hydrazine on cobalt(II) tetrasulfophthalocyanine in the absence of air results in the formation of yellow-green solutions for which only small residual paramagnetisms are detected (0.6 to 0.8 B.M.). These small values correspond to those commonly encountered in spin-paired d⁶ or d⁸ systems.¹⁰ The solutions reduced in this manner are readily oxidized back to paramagnetic states by atmospheric oxygen. The values obtained for the magnetic moments on reoxidation of the reduced systems (1.59 ± 0.04 B.M.) are substantially lower than that of the parent compound, which displays a moment of 1.88 B.M. under comparable conditions. The visible

- (1) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).
- (2) A. A. Vleck, *Nature*, **180**, 753 (1957).
- (3) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).
- (4) L. Malatesta and A. Sacco, *Z. anorg. allgem. Chem.*, **279**, 247 (1953).
- (5) K. Bernauer, P. Gaiser, O. Muller, E. Muller, and F. Gunter, *Biochem. Z.*, **338**, 560 (1961).
- (6) H. S. Mason, I. Yamazaki, T. Nakamura, and B. Allen, Abstracts of the Proceedings of the 7th International Conference on Coordination Chemistry, 1962, p. 133.
- (7) R. J. P. Williams, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 80.
- (8) S. L. Tackett, Thesis, The Ohio State University, 1962.
- (9) O. Muller and G. Muller, *Biochem. Z.*, **336**, 229 (1962).
- (10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 147.

TABLE I
MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF AQUEOUS SOLUTIONS OF COBALT(I) TETRASULFOPHTHALOCYANINE (Co(I) SPc) IN THE PRESENCE OF REDUCING AGENTS^a

System	Diamagnetism, $\chi_{\text{corr}} \times 10^6$	$\chi_M \times 10^6$ (complex)	μ_{eff} , B.M.
Co(II) SPc	+550	+940	1.88 ± 0.05
Co(I) SPc + 2Na ₂ S ^b	+618	-344	0.80 ± 0.09
Co(II) SPc + 2Na ₂ S + air ^c	+618	+368	1.53 ± 0.01
Co(II) SPc + 1Na ₂ S + air ^c	+584	+528	1.62 ± 0.05
Co(I) SPc + 2N ₂ H ₄ ^b	+569	-405	0.62 ± 0.01
Co(II) SPc + 2N ₂ H ₄ + air ^c	+569	+514	1.60 ± 0.05

^a All measurements were on 0.025 M Co SPc in water at 20°. ^b Co(II) SPc and reducing agent are pipetted into the sample tube and are mixed after the tube is tightly capped. ^c Samples air-oxidized to constant μ_{eff} value.

spectrum of the solution of the cobalt(II) complex, after reoxidation of the reduced form, is only slightly changed from that of the starting material. These complicating factors may be attributed to the formation of dimers.^{11,12} This and a number of related phenomena, including the sensitivity of the complex toward oxidation to cobalt(III) derivatives, constitute the subject of another report.^{13,13a}

The spectrum of the reduced species was obtained after electrolytic reduction in an 0.022 M phosphate buffer at pH 6.9. Solutions obtained in this way are yellow-green in color as are those produced by chemical reduction. A single broad, weak band was observed with a maximum at 643 m μ . The spectrum of cobalt(II) tetrasulfophthalocyanine exhibits strong bands at 626 and 313 m μ .¹³

It has been established that two equivalent reductions occur with cyanocobalamin producing a species that has been formulated as a hydride of cobalt(III)-B₁₂ and named hydridocobalamin^{8,9}. The spin-paired reduced species formed in the experiments reported above presumably contains cobalt in a closely related electronic state, and one might therefore expect hydridocobalamin to contain cobalt in a spin-paired condition.

The very significant question concerning whether the reduced form of cobalt tetrasulfophthalocyanine contains cobalt(I) or a hydride of cobalt(III) merits attention. Recent synthetic work on the cobalamin coenzymes has shown that hydridocobalamin is a valuable intermediate in the synthesis of compounds containing

- (11) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **44**, 1287 (1961).
- (12) H. Kobayashi, Y. Torii, and N. Fukada, *Nippon Kagaku Zasshi*, **81**, 694 (1960).
- (13) J. H. Weber, Thesis, The Ohio State University, 1963.
- (13a) NOTE ADDED IN PROOF.—Charman [*Nature*, **201**, 1021 (1964)] recently has reported the reduction of crude cobalt and other sulfophthalocyanines.

cobalt-carbon bonds.^{9,14} It has been logical to assume that the precursor contains the analogous cobalt-hydrogen bond; however, direct evidence for the presence of the hydride is lacking, although the existence of $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ has provided a precedent for the assumption.^{15,16}

Two well-established physical techniques¹⁷ offer routes to the detection of the Co-H linkage. Interferences in the region of interest in the infrared spectrum combined with the marginal stability of the reduced species have made the p.m.r. technique especially valuable in the present instance. The p.m.r. spectra have been studied on a Varian HR-60 spectrometer. The twelve hydrogen atoms on the benzene rings of the compound provide an internal means of determining the intensity to be expected for the single hydrogen resonance being sought and a check on the diamagnetism of the complex. Thus, a method is at hand for detecting oxidation with its accompanying production of paramagnetic species. Owing to the aromatic character of the phthalocyanine ring, the twelve benzene hydrogens occur 4.4 p.p.m. downfield from the water resonance. Spectra were obtained in H_2O and D_2O solutions in the presence of reducing agents in both acidic and basic media. In view of the conditions and relationships stated, the absence of the Co-H resonance in the region from 10 p.p.m. downfield to 30 p.p.m. upfield from the water resonance provides conclusive evidence against the existence of the reduced compound as a hydride of cobalt(III).

The precursor relationship of the so-called hydridocobalamin to vitamin B_{12} coenzyme suggests similar states of combination in the two. Although conflicting reports appear to indicate that the question as to whether the coenzyme contains spin-paired or spin-free cobalt is undecided,^{5,6,18} the results presented here suggest that the cobalt should be spin-paired in these highly reduced systems.

Finally, as regards the possible mode of action of the

coenzyme, it has been indicated that the attachment of the cobalt to the four nitrogen atoms of the ring, a carbon atom, and the benzimidazole group so hinders the central atom that it is not likely to bind to a substrate.¹⁹ Others have shown,²⁰ and we have observed,¹³ that hindered imidazoles, including benzimidazole, suffer greatly impaired coordinating ability as compared to imidazole itself. Further, alkyl groups are well known to exhibit *trans* effects. Consequently, the coenzyme is rather well designed to undergo substitution at the position normally occupied by the benzimidazole group. Thus, it need not be presumed that bonding to the cobalt atom during reaction is out of the question. In fact, the results reported here support the kind of mechanism proposed by Whitlock,²¹ for this requires a reduced, spin-paired state for the cobalt atom.

Experimental

Materials.—Cobalt(II) tetrasulfophthalocyanine was prepared as reported elsewhere.²²

Measurements.—Magnetic measurements were made at field strengths of 19 kgauss by the Gouy method. Details concerning the apparatus, calibration, the design of solutions, and the calculation of susceptibilities of solutes are reported elsewhere.²² Solutions for the measurements reported here were prepared by pipetting 5.00 ml. of 0.05 *M* cobalt(II) tetrasulfophthalocyanine solution and 5.00 ml. of 0.100 *M* reducing agent solution into the Gouy tube. The tube was tightly stoppered and the solution was mixed by repeatedly inverting the tube. The contents were mixed in this manner between successive Δw determinations until constant values were obtained. Oxygen was not excluded prior to closing the sample tube. Samples for p.m.r. measurements were handled similarly. A Varian Model HR-60 was used.

The visible spectrum of the reduced cobalt complex was obtained with a Cary Model 14 recording spectrophotometer, after electrolytic reduction for 15 min. at 2.5 v. (*vs.* s.c.e.).²³ The cell used for the reduction⁸ and the closed spectrophotometer cell²⁴ have been reported by other investigators.

Acknowledgment.—The investigations reported here were made possible by an unrestricted grant from the Research Corporation.

(14) E. L. Smith, L. Mervyn, A. W. Johnson, and N. Shaw, *Nature*, **194**, 1175 (1962).

(15) N. K. Kirk and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961).

(16) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

(17) J. Chatt and B. L. Shaw, "The 17th International Congress of Pure and Applied Chemistry," Vol. I, Verlag Chemie, Munich, 1960, p. 147.

(18) A. W. Johnson and N. Shaw, *Proc. Chem. Soc.*, 420 (1960).

(19) G. L. Eichhorn, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p. 54.

(20) J. N. Phillips, *Rev. Pure Appl. Chem.*, **10**, 35 (1960).

(21) H. W. Whitlock, Jr., *J. Am. Chem. Soc.*, **85**, 2343 (1963).

(22) J. H. Weber and D. H. Busch, *Inorg. Chem.*, in press.

(23) J. Abbot, The Ohio State University, private communication.

(24) T. R. Sweet and J. Zehner, *Anal. Chem.*, **30**, 1713 (1958).