Acknowledgment.—We would like to express our deep appreciation to Professor E. M. Purcell for a valuable discussion on several of the above points. This work was made possible by generous grants from E. I. du Pont de Nemours and Co., Inc., and from the Esso Education Foundation.

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RECEIVED DECEMBER 28, 1955

PARAMAGNETIC RESONANCE OF OCTACYANOTUNGSTATE(V)[1]

Sir:

The paramagnetic resonance of crystalline potassium octacyanotungstate and its aqueous solutions has been observed. A polycrystalline sample of composition $K_3W(CN)_8 \cdot 0.55H_2O$ yields a single almost symmetrical resonance at room temperature. The g value at the center of the peak is 1.98. The breadth of the peak between points of extreme slope is 30 oersteds.

An aqueous solution, approximately 0.01 M in $W(CN)_8^{---}$, yields a symmetrical resonance of three lines. The central intense line occurs at $g = 1.972$ with breadth between points of extreme slope of 9.3 oersteds. The two satellites, each of intensity $7 \pm 3\%$ of that of the central peak are separated by 52 oersteds. The central peak in all probability arises from ions containing W^{184} which has zero nuclear spin and is 86% abundant; the satellites are the hyperfine components associated with W^{183} which has spin $^1/_2$ and is 14% abundant.

The spectrum of the aqueous solution is unusual in its sharpness. Owing to rapid relaxation processes, most paramagnetic compounds of heavy elements have lines so broad at room temperature, that the resonances are not easily observed. The hyperfine coupling constant is unusually large, corresponding to a magnetic field of 6×10^5 oersteds at the tungsten nucleus. The results suggest the possible usefulness of $W(CN)_8^{---}$ in experiments involving alignment of the nuclei of some of the radioactive isotopes of tungsten.

The conventional description of $W(CN)_8^{---}$ ascribes the paramagnetism to an unpaired electron occupying a d orbital. The isotropic hyperfine interaction here described requires admixture of a configuration containing unpaired electrons in s orbitals.[2] Further experiments with dilute solid solutions of $W(CN)_8^{---}$ in single crystals of a diamagnetic substance are required for more complete determination of the nature of the electronic wave function.

An attempt was made to measure the rate of electron exchange between $W(CN)_8^{---}$ and $W(CN)_8^{---}$ by the observation of the spectrum of the former in the presence of the latter. At concentrations of $W(CN)_8^{---}$ lower than 0.02 M no broadening of the hyperfine components of $W^{183}(CN)_8^{---}$ was observed. With $W(CN)_8^{---}$ at 0.04 M a slight broadening, of the order of one oersted, was observed. If the broadening arises from the electron exchange reaction, the rate constant for the bimolecular exchange is 4×10^8 liter mole^{-1}sec.$^{-1}$. The absence of broadening at lower concentrations establishes this value as an upper limit, *i.e.*, $k \leqslant 4 \times 10^8$ liter mole^{-1}sec.$^{-1}$. Previous work with radioactive tracers[3,4] has indicated that $k > 4 \times 10^4$ liter mole^{-1}sec.$^{-1}$.

(1) This work has been supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command and by the United States Atomic Energy Commission under Contract AT(11-1)-34 with the University of California.

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RECEIVED FEBRUARY 6, 1956

THE PARTIAL STRUCTURE OF NOVOBIOCIN (STREPTONIVICIN).[1] II.

Sir:

The isolation and properties of novobiocin have been described.[2-4] The present studies, added to those previously reported,[5] indicate that it is a C_9 sugar attached glycosidically to the 7-position of 3-[4-hydroxy-3-(3-methyl-2-butenyl)-benzamido]-4,7-dihydroxy-8-methylcoumarin.

Novobiocin (I) ($C_{31}H_{36}N_2O_{11}$), is cleaved by the action of hot acetic anhydride to yield 4-acetoxy-3-(3-methyl-2-butenyl)-benzoic acid (II) and a neutral compound, $C_{23}H_{26}N_2O_{10}$ (III).[5] Hydrolysis of I by 4 N hydrochloric acid in 60% ethanol gave an optically inactive acid, $C_{22}H_{21}NO_6$ (IV), which upon cleavage with hot acetic anhydride yielded 2,2-dimethyl-6-chromancarboxylic acid (VI) and an optically inactive neutral compound, $C_{14}H_{11}NO_5$ (VII).[5]

In addition to IV, the acid hydrolysis affords an

(1) The Upjohn Company Registered Trade Mark for novobiocin is Albamycin. Our previous Communication[5] on the structure of this antibiotic is listed under our former generic name, streptonivicin, now abandoned. The isolation of the same material by the Merck group has been described in THIS JOURNAL, **77**, 6404 (1955). The comparisons establishing identity are described by Henry Welch and W. W. Wright in *Antibiotics and Chemotherapy*, **5**, 670 (1955).

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