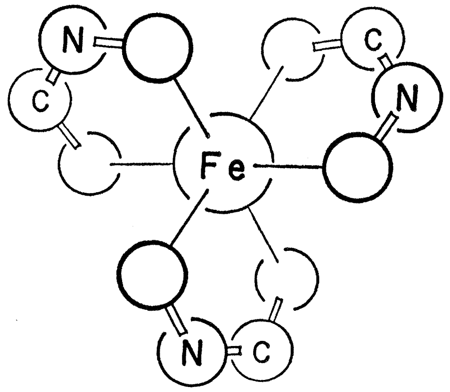

Fig. 3. Absolute configuration around the iron atom.

a time could be occupied. The oxygen atom of one serine side chain, the methyl carbon and α-carbon of one methyl glutaconic acid residue, and the oxygen atoms of the terminal carboxyl group of another glutaconic acid were each assigned two sites corresponding to two ways of twisting each of these groups. An electron-density-difference function calculated at this point showed peaks which can be explained as the result of either anisotropic thermal motion or slight shifts associated with the disorder of neighboring atoms. Other peaks were found in correct positions for about 40 hydrogen atoms on those parts of the structure for which the effects of disorder and anisotropic motion are less severe. Further calculations taking account of these hydrogen atoms and some of the anisotropic motion effects have reduced R to 0.09.

The molecular shape is shown in Fig. 2. The sequence of amino acid residues (ornithine, serine, and glycine) in the cyclic peptide is -Orn-Orn-Orn-Ser-Ser-Gly-. The conformation of the ring is *trans* at each peptide linkage. The absolute configuration of each of the five asymmetric α-carbon atoms is the same as that commonly found in other peptides of biological origin and is described conventionally as left-handed. The absolute configuration of the three hydroxamate rings at the iron atom (Fig. 3) is that of a left-handed propeller. In such a ring structure there are two distinct ways in which the polarities of the C—N bonds can be arranged, either all the same way or one different from the other two. We find the more symmetrical structure in which the polarities are the same in the three rings, as shown in Fig. 3.

We recognize two hydrogen bonds within the molecule. One of length 2.99 Å bridges the peptide ring and joins the α-nitrogen of one ornithine residue to the carbonyl oxygen of one serine residue. This bond distance corresponds to a weak bond. In the flat representation of this ring (Fig. 1) there seems to be the possibility of a second hydrogen bond across the ring, but the folding of the ring in the actual structure does not permit this. A second hydrogen bond of length 2.79 Å joins the α-nitrogen of the second ornithine residue to the oxygen atom of the δ-nitrogen of this same residue.

Several other hydrogen bonds connect various oxygen atoms with water molecules which in turn are connected to other ferrichrome molecules. There is disorder in some of these bonds, because they involve some of the atoms with alternate sites.

Bond distances and angles which do not involve hydrogen atoms are in good agreement with the expected values, with standard deviations of the distances being approximately 0.02 Å. The six oxygen neighbors of the iron atom are at distances ranging from 1.96 to 2.07 Å. The bond angles at the iron atom which would be 90° for a regular octahedron range from 78° to 101°.

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6. We thank Prof. J. B. Neilands for providing the crystals for this investigation and for helpful discussions concerning the molecular structure. This work was done under the auspices of the AEC.

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Sodium Perxenate and Xenon (II) Difluoride Reduction at the Dropping-Mercury Electrode

Abstract. *Sodium perxenate in alkaline solutions is reduced in a single step to xenon at the dropping-mercury electrode. The half-wave potential for perxenate changes from −0.21 to −0.31 volts against a Hg_2SO_4–Hg reference electrode in the* pH *range 10.1 to 11.3. Xenon (II) difluoride in acidic solution is reduced in a single step to xenon, at the potential of approximately zero against the Hg_2SO_4–Hg reference electrode. The reduction wave is followed by a broad maximum which can be effectively suppressed by fluoride ion. The diffusion current varies in linear fashion with concentration.*

Investigation of perxenate and xenon (II) difluoride reduction at the dropping-mercury electrode was undertaken to learn whether these compounds are reduced directly to xenon, as has been observed for the xenic acid by Jaselskis (*1*), or whether perxenate undergoes a stepwise reduction.

Table 1. Polarographic characteristics of sodium perxenate and xenon (II) difluoride. The *p*H is that of the supporting electrolyte; abbreviations are: *i*, diffusion current; *C*, concentration of xenon compound; *m*, mass of flow of mercury (mg/sec); and *t* is drop time (sec).

Concn ($10^{-5}M$)	*p*H	$E_{\frac{1}{2}}$ vs Hg_2SO_4–Hg (v)	*i* (μa)	$i/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$
		Xenic acid		
9.1	6.4*	−0.32	1.06	7.71
		Sodium perxenate		
14.1	11.3†	− .31	2.10	9.86
14.1	10.1‡	− .21	2.05	9.63
14.1	3.0+§	.0	1.56	7.33
17.1	11.3†	− .31	2.55	9.93
17.1	3.0+§	.0	1.90	7.40
		Xenon (II) difluoride		
17.3	4.5‡‖	.0	0.58	2.23
34.7	4.5‡‖	.0	1.25	2.40
69.5	4.5‡‖	.0	2.55	2.44

* Unbuffered 0.1*M* potassium sulfate. † 0.1*M* potassium sulfate and 0.001*M* sodium hydroxide. ‡ 0.1*M* potassium sulfate and 0.005*M* sodium carbonate and bicarbonate. § Acidified solution of sodium perxenate in 0.1*M* potassium sulfate. ‖ 0.1*M* potassium sulfate, 0.02*M* acetic acid, and 0.02*M* sodium acetate or 0.1*M* potassium sulfate, 0.02*M* acetic acid, 0.02*M* sodium acetate, and 0.1*M* sodium fluoride.

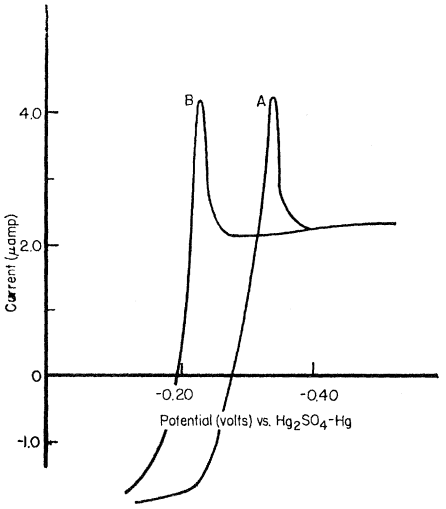

Fig. 1. Polarogram of $1.41 \times 10^{-4}M$ sodium perxenate in a mixture of $0.1M$ potassium sulfate and $0.001M$ NaOH (curve A), and in a mixture of $0.1M$ potassium sulfate and $0.005M$ sodium carbonate–sodium bicarbonate (curve B).

The preparation of the stable sodium perxenate salt, $Na_4XeO_6 \cdot 2H_2O$, and the aqueous solution chemistry of xenon (VIII) has been described by Malm *et al.* (*2*) and Appelman and Malm (*3*). Xenon (II) difluoride has been prepared by Weeks *et al.* (*4*), and the characterization of the aqueous solutions of xenon (II) difluoride has been described by Appelman and Malm (*5*).

A Sargent XXI recording polargraph and H-polarographic cell equipped with a thermostat were used for the polarographic study. The temperature of the H-cell was kept at 2°C by circulating ice-cold water. Sodium acetate, acetic acid, and $0.1M$ potassium sulfate, with or without sodium fluoride buffer solutions, were used for the study of xenon (II) difluoride. Sodium perxenate was studied in $0.1M$ potassium sulfate and $0.001M$ NaOH or in $0.1M$ potassium sulfate and $0.005M$ sodium carbonate–bicarbonate supporting electrolytes.

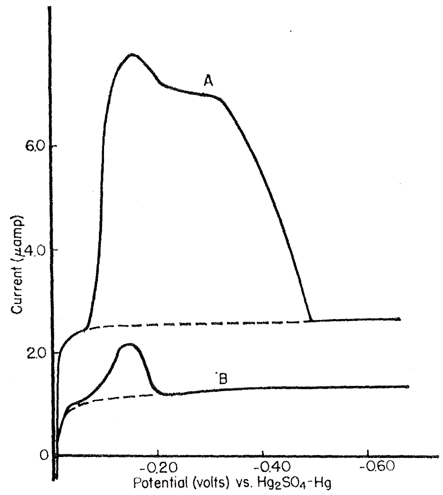

Fig. 2. Polarograms of xenon (II) difluoride. Solid lines, in $0.1M$ potassium sulfate and $0.04M$ acetic acid–$0.02M$ sodium acetate; dashed lines, in $0.1M$ potassium sulfate, $0.1M$ sodium fluoride, and $0.04M$ acetic acid–$0.02M$ sodium acetate. Concentration of xenon (II) difluoride $6.95 \times 10^{-4}M$ (curve A) and $3.47 \times 10^{-4}M$ (curve B).

A known amount of sodium perxenate was added directly to a measured volume of deaerated supporting electrolyte in the polarographic cell. In this manner it was possible to minimize the decomposition of perxenate and to vary the concentration. After the polarogram was recorded one drop of $1.0M$ sulfuric acid was added to the polarographic cell to decompose the perxenate to xenic acid ($XeO_3 \cdot xH_2O$) and after deaeration for 2 minutes, a second polarogram was recorded.

The aqueous stock solutions of xenon (II) difluoride were preserved by freezing the solutions. The concentration of XeF_2 was varied by taking portions of melted xenon (II) difluoride solution and recording the polarograms immediately after deaeration of the solution by nitrogen which had been purified by passing over hot copper turnings. The deaeration was carried out in the absence of mercury to prevent the reduction of perxenate and xenon (II) difluoride. The xenon (II) difluoride concentration in the concentrated stock solution was determined iodometrically.

Typical polarograms of perxenate and of xenon (II) difluoride are shown in Figs. 1 and 2, and the results are summarized in Table 1.

In the potassium sulfate and $0.001M$ sodium hydroxide electrolyte, sodium perxenate shows a well-defined cathodic wave preceded by an anodic portion of the wave which can be attributed to the formation of an insoluble mercuric oxide that has been previously observed by Kheirovskii and Trifonov (*6*). The cathodic portion of the wave corresponds to an eight-electron reduction process. The number of electrons taking part in the reduction process has been calculated by a comparison of the periodate reduction to iodate and xenic acid reduction to xenon. Since sodium perxenate is readily decomposed in acid solution to xenic acid, the polarograms of perxenate in alkaline solution and in acid solution yield values for the diffusion current differing by the amount of the current equivalent to a two-electron change.

For the same concentration, the reduction wave of perxenate is four times greater than that of periodate and 1.33 times greater than that of xenic acid. The half-wave potential, $E_{\frac{1}{2}}$, becomes more negative with increasing pH, as would be expected for the reduction reaction

$$HXeO_6^{-3} + 11\ H^+ + 8e = Xe^0 + 6H_2O$$

For a reversible process at 2°C the change of pH by one unit should produce a shift of the half-wave potential by 0.075 as observed 0.083 volt.

In the buffer composed of potassium sulfate, sodium acetate, and acetic acid, xenon (II) difluoride is reduced in the vicinity of 0 volts measured against a Hg_2SO_4–Hg reference electrode. The reduction is followed by a broad maximum, which can be suppressed by the fluoride ion. For the same concentration, the reduction current for xenon (II) difluoride is approximately one-third that of xenic acid. The reduction of xenon (II) difluoride is highly irreversible, and is greatly influenced by the fluoride ion.

The cathodic current for sodium perxenate is proportional to the square root of mercury head, and changes by approximately 2.5 percent per degree Celsius, indicating that the reduction process is primarily diffusion controlled. The reduction of xenon (II) difluoride in $0.1M$ sodium fluoride, sodium acetate, and acetic acid electrolyte is diffusion controlled. However, in the absence of appreciable concentration of fluoride the reduction wave and the broad maximum appear to be adsorption type.

The cathodic current of sodium perxenate and xenon (II) difluoride is directly proportional to concentration.

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