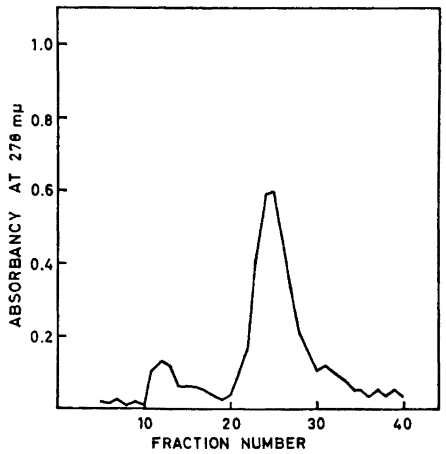

Fig. 1. Separation of aqueous ethanol extract of ram seminal plasma by silicic acid chromatography. Column 5 g. Fraction 15 ml. Ethyl acetate:benzene was used as the eluent in the following ratios: Fractions 1 to 10, 20:80; Fractions 11 to 20, 30:70; Fractions 21 to 30, 60:40; Fractions 31 to 40, 80:20.

After treatment with alkali (0.5 NaOH) and measuring the ultraviolet absorption at 278 mμ only one peak was found corresponding to the PGE-compounds. No or only slight ultraviolet absorption was found in the fractions eluted with ethyl acetate:benzene, 30:70, and 80:20, indicating the absence of 19-hydroxylated prostaglandins in ram semen (Fig. 1).

These studies therefore show that ram seminal plasma as human contains five prostaglandins PGE_1, PGE_2, PGE_3, $PGF_{1\alpha}$, and $PGF_{2\alpha}$ although the concentration of PGE_2 was lower than in human semen. In difference to human semen 19-hydroxylated prostaglandins could not be demonstrated in ram semen.

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On the Crystal Structure of Bis-L-histidine-copper(II) Dinitrate Dihydrate

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An investigation of the crystal structure of biochemically interesting metal complexes has been started in conjunction with the Department of Biochemistry at this University. In this communication the preliminary results of a crystal structure determination of the bis-L-histidine-copper-(II) dinitrate dihydrate are presented.

The crystals were prepared according to a method described by Valladas-Dubois,[1] whereby a concentrated solution of $CuSO_4$ was mixed with a concentrated solution of L-histidine so as to give a Cu(II):histidine molar ratio of 1:2. A large excess of solid $NaNO_3$ was dissolved in the resulting solu-

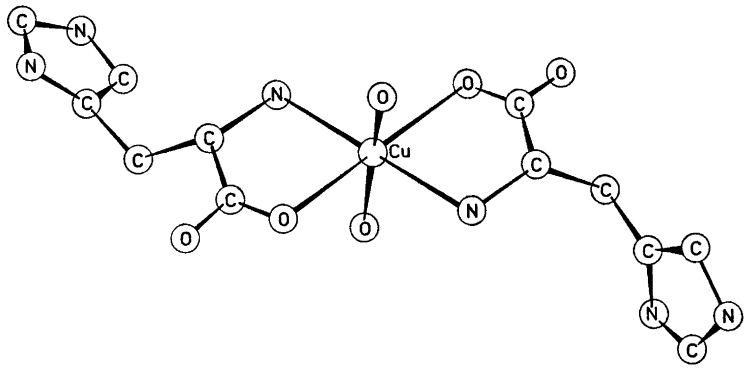

Fig. 1.

tion whereupon clusters of blueviolet needle-shaped crystals of $[(C_6H_9O_2N_3)_2Cu](NO_3)_2(H_2O)_2$ were slowly deposited. An analysis of the crystals yielded 27.0 % C, 20.8 % N, and 4.13 % H which is in good agreement with the theoretical values 27.0 % C, 21.0 % N, and 4.15 % H. A sample decomposed by 0.5 M HCl showed a specific rotation of + 11.0° which is close to the specific rotation of pure L-histidine in 0.5 M HCl, + 11.1°.[2]

The layers ($0kl-4kl$) were recorded with Cu$K\alpha$ radiation using multiple film Weissenberg techniques, the crystal being mounted with its needle-axis as rotation axis. A crystal cut to a suitable size was used to register the layers ($hk0-hk10$). The crystals were found to be triclinic with cell dimensions $a = 5.47$ Å, $b = 7.13$ Å, $c = 13.84$ Å, $\alpha = 97°$, $\beta = 86°$, and $\gamma = 109°$ as calculated from the Weissenberg data. The volume of the unit cell is 506 Å^3, corresponding to one formula unit of $[(C_6H_9O_2N_3)_2Cu](NO_3)_2(H_2O)_2$. This gives a calculated density of 1.75 g/cm^3 as compared with the observed value of 1.77 g/cm^3.

A positive piezo-electric test and the fact that the complex contains two L-histidine molecules indicates that the correct space group is the non-centrosymmetric No. 1 $-P1$.[3]

Since there is only one copper atom in the unit cell, it was arbitrarily assigned the position $P1$:1(a) with $x = 0$, $y = 0$, and $z = 0$. A three-dimensional electron density summation based on this copper position and the $0kl-4kl$ Weissenberg data, scaled together using the Weissenberg photograph $hk0$, was calculated, from which the coordination about the copper atom and the main features of the histidine molecules could be discerned. Successive electron density calculations revealed approximate positional parameters of all atoms in the unit cell excluding hydrogen atoms. A least squares refinement of these parameters using the $0kl-4kl$ data gave an R value of 14.8 % and reasonable isotropic temperature factors. A least squares refinement of the complete three-dimensional data is now in progress.

The most interesting feature of the structure, is that two neutral histidine molecules are coordinated to the central copper atom each through the amino nitrogen and a carboxylate oxygen and not through the imidazole group (*cf.* Fig. 1). The coordination about copper is square planar, the Cu—O and Cu—N distances being approximately 2.0 Å. There are two water molecules one above and one below the plane at distances of 2.5 Å and 2.8 Å.

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