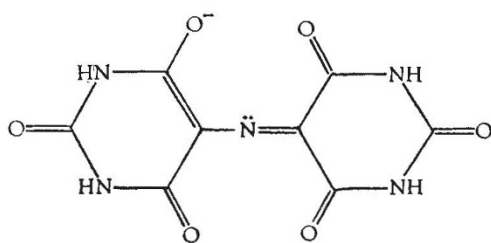(a)

(b)

conjugated system, but would require that the non-bonding electrons of the central nitrogen atom occupied a pure p-orbital, a situation for which there is no precedent.

It was hoped that crystallographic symmetry of a purpurate might permit a decision between (a) and (b). In (a), the ion could possess at most a plane of symmetry. Moreover, the plane of one ring would be an almost perpendicular bisector of the other (negatively charged) ring, and it seems unlikely that such a molecule would be disordered in the crystal. In (b), on the other hand, the molecular symmetry could be as high as D_{2h}.

Potassium purpurate was crystallized from aqueous solution as black, rectangular needles of the dihydrate, which were examined by means of precession photographs and found to be orthorhombic with $a = 7 \cdot 39 \pm 0 \cdot 03$, $b = 16 \cdot 47 \pm 0 \cdot 10$, $c = 21 \cdot 80 \pm 0 \cdot 20$, and eight molecules in the unit cell (density $1 \cdot 76 \pm 0 \cdot 02$; calculated, $1 \cdot 72 \pm 0 \cdot 04$). The space group $Ibca$ was uniquely determined by systematic absences. It follows that the bridging nitrogen atoms lie either at inversion centres or on twofold rotation axes, and thus that either the rings are equivalent, or the bridge is linear, or both (unless the structure is disordered, for which there is no evidence at present).

Although this result does not permit a conclusive decision on the point at issue, it is consistent with the planar–linear structure (b), and cannot easily be reconciled with (a) or any other reasonable one. In view of the interesting stereochemical consequences, a complete structure determination is now being undertaken.

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Gel Growth of Crystalline Cuprous Chloride

MURRAY[1] has predicted that crystalline cuprous chloride may be of use as a modulator material in lasers. Crystals of this material are generally grown from the melt[2], but the method has certain disadvantages. First, the presence of a phase transition[2] 15° C below the melting point (422° C) produces strains in the resulting crystals. This is further intensified by temperature gradients produced in the crystal during cooling from the melting point to room temperature. Contamination from container materials is another hazard. We have endeavoured to eliminate these undesirable influences by growing cuprous chloride at room temperature with a variation of the gel growth technique.

In this method, the crystals are grown in contact with only a porous gel and a nutrient solution and thus should not encounter any strain due to pressure from the immediate environment. Gel growth usually involves crystal growth by diffusion of ions through a gel sandwiched between solutions containing the ions to be combined or into a gel which contains one of the reactants. In the method used here, however, the growth depends only on the migration of the chloride ion from an acid solution of cuprous chloride.

It is well known that cuprous chloride forms a soluble complex in fairly strong hydrochloric acid solution, but that this complex is unstable in dilute acid which leads to the precipitation of cuprous chloride. In this work, a gel was used to control the loss of the chloride ion, and thus allowance was made for the slow precipitation of cuprous chloride which resulted in the formation of crystalline material.

Experimentally, the gels were prepared by titrating 1 N hydrochloric acid with $0 \cdot 5$ M sodium metasilicate to the required pH. All solutions had previously been passed through $0 \cdot 45\mu$ 'Millipore' filters in order to eliminate any particles which might serve as nucleation sites. The gels were allowed to set overnight in test-tubes at 40° C. About 10 c.c. of solution of hydrochloric acid saturated with cuprous chloride was then placed over about 25 c.c. of gel, stoppered and allowed to react in the dark at room temperature.

Briefly, the results were as follows. The normality of the hydrochloric acid solutions varied from 6 to $0 \cdot 75$. No crystals were formed when the normality was below 3; fine crystalline material resulted from 3 N hydrochloric acid solutions. The best crystals were formed from 6 N hydrochloric acid solutions. On one occasion a single tetrahedron resulted from a 6 N solution, which was about 3/8 in. on each side. The pH of the gel did not seem to have any observable effect on the product. The pH's were varied from $3 \cdot 5$ to $4 \cdot 5$. The reaction time was 3 weeks. The best crystals were skeletal in form, containing long, narrow voids, and were not water clear. X-ray examination (Laue back reflexion) produced spots which were rather diffuse indicating the material is not a single crystal.

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Exceptionally Calcic Pyralspite from South African Kyanite Eclogite

PYRALSPITE garnets with C ($= Ca/Ca + Mg + Mn + Fe^{2+}$) > $0 \cdot 35$ are rare. Some authors[1] postulate a miscibility gap between garnets of composition $C < 0 \cdot 35$ and the ugrandite series with $C > 0 \cdot 70$. The alternative, that garnets with $0 \cdot 35 < C < 0 \cdot 70$ are stable but crystallize, under suitable physical conditions, only from rarely encountered silica-poor bulk compositions, has also been suggested[2]. This hypothesis is supported by the synthesis of a complete series of garnets ($C = 0$–$1 \cdot 0$) between pyrope and grossularite at 30 kbars and $1,200^\circ$ C (ref. 3). The synthetic garnets with C values between $0 \cdot 5$ and $0 \cdot 7$ are of particular interest because at 30 kbars and $1,600^\circ$ C these