The Structure of the Tris(pentasulphido)platinum(IV) Anion

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CRYSTALS of $(NH_4)_2PtS_{15}, 2H_2O$ were prepared for us and the structure problem suggested to us by Professor R. A. Krause of this department. The preparative method used was that of Hofmann and Höchtlen.¹ The crystals are monoclinic with a = 15.77, b = 9.99, c = 13.01 Å and $\beta = 93.7^{\circ}$. The space group is Cc, and there are four formula units per unit cell. The structure determination was based on 1340 independent reflections measured visually from equi-inclination Weissenberg photographs taken with Ni-filtered Cu radiation.

The x and z co-ordinates for platinum were taken arbitrarily and the y co-ordinate was found from a Patterson synthesis. The three-dimensional electron density map using phases based on platinum alone was calculated. Since this map was essentially the electron density map of the structure and its centre-related structure, the sulphur atoms were found through structural considerations and the use of successive non-centrosymmetric electron density maps in which the redundant atoms were gradually eliminated. The structure is being refined by Busing, Martin, and Levy's full-matrix least-squares programme. The unweighted reliability index, R, using anisotropic temperature parameters is 13%. Only one water molecule has been located; a second may be distributed randomly, but no positive evidence for placing a second water molecule has been obtained from the structure work thus far.



FIGURE. Configuration of PtS₁₅²⁻.

The anion consists of three five-membered sulphur chains co-ordinated to a central platinum atom so as to form, with platinum, three sixmembered rings in chair configurations. This is illustrated in the Figure. The co-ordination environment for platinum is octahedral. At the present time the bond length and angle ranges, average values, and estimated standard deviations of individual values are: Pt-S, $2\cdot28-2\cdot54$, $2\cdot43$, $0\cdot03$ Å; S-S, $1\cdot98-2\cdot15$, $2\cdot05$, $0\cdot05$ Å; S-S-S,

¹ K. A. Hofmann and F. Höchtlen, Ber., 1903, 36, 3090.

97.8—116.1, 104.8, 5°; Pt-S-S, 103.0—113.0, 109.4, 2.5°; S-Pt-S, 90.5—96.4, 92.8, 2.5°.

Financial support from the National Science Foundation and a N.A.S.A. predoctoral fellowship (to P. E. J.) are gratefully acknowledged.

(Received, July 3rd, 1967; Com. 687.)