

I have found (Tang, 1950) that the data for this phase, which covers the composition range 63–88% of platinum, are compatible with a cubic structure of the type ABC_6 with

A at $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0) + 0, 0, 0;$

B at $+\frac{1}{2}, 0, 0;$

and C at $+\frac{1}{4}, \frac{1}{4}, 0; +0, \frac{1}{4}, \frac{1}{4}; +\frac{1}{4}, 0, \frac{1}{4}; +\frac{1}{4}, \frac{1}{4}, \frac{1}{2};$
 $+\frac{1}{2}, \frac{1}{4}, \frac{1}{4}; +\frac{1}{4}, \frac{1}{2}, \frac{1}{4},$

as shown in Fig. 1. The structure factors for the three types of unmixed hkl are:

$F_{hkl} = 4(f_A + f_B + 6f_C)$, if hkl are all multiples of 4, or all even but not divisible by 4;

$F_{hkl} = 4(f_A + f_B - 2f_C)$, if hkl are all even and only one or two of them are divisible by 4;

$F_{hkl} = 4(f_A - f_B)$, if hkl are all odd.

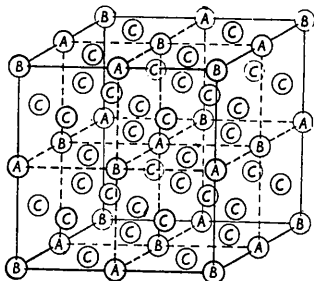
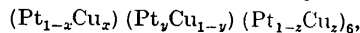


Fig. 1. The cubic structure ABC_6 , $Z = 4$.

For the alloy containing 72.5% of platinum A is Pt, B is Cu and C is the statistical atom ($Pt_{0.8}Cu_{0.2}$). The cubic structure $PtCu(Pt_{0.8}Cu_{0.2})_6$ gives at least as good agreement with X-ray intensities as Schneider & Esch's structure. The calculated intensities and those observed by Schneider & Esch are given in Table 1.

It is not particularly surprising that the alloy in question, which corresponds to a maximum in the electric-conductivity-composition curve and which gave maximum intensities to superstructure lines (Schneider & Esch, 1944) contains the statistical atom ($Pt_{0.8}Cu_{0.2}$). As a matter of fact it is the composition ($Pt_{0.8}Cu_{0.2}$) Cu_3 in the cubic phase of nominal composition $PtCu_3$ which corresponds to a high peak in the conductivity diagram and also gives maximum intensities to superstructure lines (Schneider & Esch, 1944; Johansson & Linde, 1927). The statistical atom ($Pt_{0.8}Cu_{0.2}$) may involve some short-range order which is not detectable by ordinary X-ray diffraction methods.

The complex conductivity and X-ray data for the other alloys between 63 and 88% of platinum in the cubic phase of nominal composition $PtCuPt_6$ are understandable in terms of cubic structures as described by the formula



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Structure studies of the two forms of sodium tripolyphosphate. By J. J. DYMOM and A. J. KING, *Department of Chemistry, Syracuse University, Syracuse 10, New York, U.S.A.*

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Sodium tripolyphosphate, $Na_3P_3O_{10}$, is the only crystalline polyphosphate which has been observed as an inter-

mediate phase in the binary system $Na_3P_3O_9$ – $Na_4P_2O_7$. Its existence has been substantiated by a number of

Table 1. *Calculated and observed intensities for*
 $PtCu(Pt_{0.8}Cu_{0.2})_6$

hkl	$\sin \theta$	$PLHF^2 \times 10^{-6}$	I
111	(0.173)	9	—
200	(0.200)	2	—
220	0.284	2	<i>vw</i>
311	0.335	11	<i>vw</i>
222	0.347	350	<i>ms</i>
400	0.402	200	<i>mw</i>
331, 402	0.441	11	<i>vw</i>
224	(0.510)	2	—
333, 511	0.528	8	<i>vw</i>
440	0.565	250	<i>s</i>
531	0.592	10	<i>vw</i>
600, 442	(0.600)	2	—
620	(0.632)	2	—
335	0.653	5	<i>vwv</i>
622	0.663	410	<i>vs</i>
444	0.691	135	<i>m</i>
551, 711	0.713	10	<i>vw</i>
406	(0.720)	2	—
624	0.749	4	<i>vwv</i>
731, 553	0.768	15	<i>vw</i>
800	0.798	113	<i>mw</i>
733	0.818	6	<i>vw</i>
802, 446	0.830	5	<i>vwv</i>
228, 660	0.845	3	<i>vwv</i>
555, 157	0.864	16	<i>w</i>
662	0.870	626	<i>vs</i>
840	0.893	680	<i>vs</i>
911, 735	0.910	28	<i>w</i>
842	(0.917)	7	—
664	(0.938)	4	—
913	0.952	29	<i>vw</i>
844	0.978	2110	<i>vs</i>

P = polarization factor; L = Lorentz factor; H = multiplicity factor. m = moderate; s = strong; v = very; w = weak.

In view of the fact that there is no detectable splitting of the cubic lines and of the satisfactory agreement with X-ray intensities given by the cubic structure $PtCu(Pt_{0.8}Cu_{0.2})_6$, this structure is probably the correct one for the annealed Pt–Cu alloy containing 72.5% of platinum, and the cubic phase covering the entire range of 63–88% of platinum is probably similarly based upon the cubic structure ABC_6 .

I wish to thank Prof. Linus Pauling for suggesting this problem to me, and for many helpful discussions.

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investigators (Andress & Wüst, 1938, 1939; Partridge, Hicks & Smith, 1941; Ingerson & Morey, 1943; Morey & Ingerson, 1941) using thermal, microscopic, X-ray diffraction and molecular-weight-determination methods. The phase diagram (Partridge *et al.* 1941; Morey & Ingerson, 1941) shows that it melts incongruently at 620–622°C. to form a liquid phase and crystalline sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$. Over the range of compositions between 33 and 48% $\text{Na}_4\text{P}_2\text{O}_7$, crystalline $\text{Na}_5\text{P}_3\text{O}_{10}$ separates as the primary phase. It exists in two crystalline forms, as demonstrated by powder diffraction patterns (Partridge *et al.* 1941) and by measurements of the optical properties (Ingerson & Morey, 1943).

In the present investigation small crystals of $\text{Na}_5\text{P}_3\text{O}_{10}$ (I) were obtained by cooling the melt (of composition corresponding to 45% $\text{Na}_4\text{P}_2\text{O}_7$, 55% $\text{Na}_3\text{P}_3\text{O}_9$) from 640 to 565°C. at a rate of 2°C./hr., finally quenching in a bath of dry ice and acetone. If, however, the cooling of the melt was continued to 500°C. before quenching, single crystals of $\text{Na}_5\text{P}_3\text{O}_{10}$ (II) could be isolated from the partially powdered mass. Simulated powder patterns were produced from these single crystals in a manner which did not destroy them for further study by single-crystal methods. The powder patterns so obtained verified the identity of the two forms as previously reported.

X-ray data were obtained by Weissenberg and oscillation methods. $\text{Na}_5\text{P}_3\text{O}_{10}$ (I) is monoclinic with

$$a = 9.73 \pm 0.02, \quad b = 5.41 \pm 0.02, \quad c = 19.97 \pm 0.02 \text{ \AA.}, \\ \beta = 112^\circ 12'.$$

The density determined by the flotation method is 2.52 g.cm.⁻³ (calculated 2.51 g.cm.⁻³), hence the cell contains four molecules. Reflections were systematically absent for (*hkl*) with (*h+k*) odd, (*h0l*) with *h* and *l* odd, (*0k0*) with *k* odd. The space group therefore is either *C2/c* or *Cc*. Samples tested by Dr R. G. Stokes of the Naval Research Laboratory, Washington, D.C., failed to show measurable piezoelectric activity, thus making it impossible to decide with certainty between these two space groups.

$\text{Na}_5\text{P}_3\text{O}_{10}$ (II) is also monoclinic with

$$a = 16.08 \pm 0.02, \quad b = 5.24 \pm 0.02, \quad c = 11.28 \pm 0.02 \text{ \AA.}, \\ \beta = 93^\circ 30'.$$

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Note on the crystalline structures of the methyl cyanide-boron trihalides. By S. GELLER* and O. N. SALMON†, *Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.*

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Crystals of $\text{H}_3\text{CCN}-\text{BCl}_3$ and $\text{H}_3\text{CCN}-\text{BBr}_3$ grown in glass capillaries as described in the paper on $\text{H}_3\text{CCN}-\text{BF}_3$ (Hoard, Owen, Buzzell & Salmon, 1950) were photographed with *Cu K α* radiation. The orthorhombic unit cells all give vanishings characteristic of the space groups

The density, found to be 2.59 g.cm.⁻³ (calculated 2.58 g.cm.⁻³), requires four molecules in the cell. No reflections were observed for (*hkl*) with (*h+k*) odd, (*h0l*) with *h* and *l* odd, and (*0k0*) with *k* odd. The space group could therefore be either *C2/c* or *Cc*, but since no piezoelectric effect could be detected, again, no decision could be made between them.

The space group *C2/c* provides eight general equivalent positions. Since the cells of both forms of $\text{Na}_5\text{P}_3\text{O}_{10}$ contain only four molecules it would be necessary for the $\text{P}_3\text{O}_{10}^{5-}$ ion to possess either a center or a twofold axis of symmetry in order to be compatible with this space group. Although it is impossible for three PO_4 tetrahedra to combine to form an ion with a center of symmetry, several arrangements exhibit twofold symmetry. These ions could lie in the set of special positions (*Internationale Tabellen* (1935), vol. 1, p. 101) at (*e*) which has twofold symmetry.

Preliminary studies indicate that both forms crystallize in *C2/c* and consist of open chains of three PO_4 tetrahedra linked by single oxygen bridges. The ion in each form probably lies at $0, y, \frac{1}{2}$; $0, \bar{y}, \frac{3}{2}$; $\frac{1}{2}, \frac{1}{2} + y, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2} - y, \frac{3}{2}$.

A complete study of these structures is now in progress.

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$D_{2h}^{16}-Pnma$ and C_{2v}^9-Pna . The lattice constants obtained are:

	<i>a</i> (Å.)	<i>b</i> (Å.)	<i>c</i> (Å.)
$\text{H}_3\text{CCN}-\text{BF}_3$	7.76	7.20	8.34
$\text{H}_3\text{CCN}-\text{BCl}_3$	8.72	7.30	10.20
$\text{H}_3\text{CCN}-\text{BBr}_3$	8.91	7.51	10.94

The pycnometric densities of $\text{H}_3\text{CCN}-\text{BF}_3$ and $\text{H}_3\text{CCN}_3-\text{BCl}_3$ are very nearly the same (Laubengayer & Sears, 1945), and there are four molecules in each of the unit cells. As far as can be ascertained $\text{H}_3\text{CCN}-\text{BBr}_3$ has not been reported elsewhere in the literature and the

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