

Phase Studies and Compound Formation in the Phosphazene and 1,3,5-Triazine Systems

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PHASE diagram techniques establish that molecular addition compounds are formed in the solid state between various chlorophosphazenes and aminophosphazenes. Addition compounds of this type have not been reported previously¹ although phase diagrams of some other binary mixtures have been investigated.²

A single eutectic occurs at 0.65 mole of $N_3P_3Cl_6$ in binary mixtures $N_3P_3Cl_6$ - $N_4P_4Cl_8$, and the

absence of compound formation² in this system is confirmed. Some mixtures of chloro- and aminocyclotriphosphazatrienes exhibit two eutectics and a well-defined maximum. An example from the cyclotetraphosphazetetraene series exhibits three eutectics and two maxima. Solid addition compounds are formed also in the 1,3,5-triazine system. A phase diagram of cyanuric chloride-hexamethylmelamine shows two maxima at temperatures

¹ R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

² A. M. de Ficquelmont, *Ann. chim. (France)*, 1939, **12**, 169.

considerably higher than the m.p.s. of either component.

The compositions and m.p.s. of typical addition compounds are recorded in the Table. The bonding in all these compounds is probably of the charge-transfer type reported for cyanuric chloride crystals.³

Compound	M.p. (°C)
$N_3P_3Cl_6, 3N_3P_3(NMe_2)_6$	114
$N_3P_3Cl_6, 3N_3P_3(NHPr^1)_6$	173
$N_3P_3Cl_4(NHBU^t)_2, 2N_3P_3Cl_2(NHBU^t)_4$	108
$N_4P_4Cl_8, 2N_4P_4(NMe_2)_8$	116
$4N_4P_4Cl_8, N_4P_4(NMe_2)_8$	122
$3N_3C_3Cl_3, N_3C_3(NMe_2)_3$	231
$N_3C_3Cl_3, 3N_3C_3(NMe_2)_3$	221

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³ O. Hassel and C. Rømming, *Quart. Rev.*, 1962, **16**, 1.