

## NOTIZEN

**The Dimeric Phosphinimine Complex  
[CdI<sub>2</sub>(HN:PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> Containing N-H...I  
Hydrogen Bonds**

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Triphenylphosphinimine and cadmium iodide form a complex containing the dimeric molecule [CdI<sub>2</sub>HN:PPh<sub>3</sub>]<sub>2</sub>. These dimers are centrosymmetric, with an eight membered ring containing the hydrogen bonded system N-H...I.

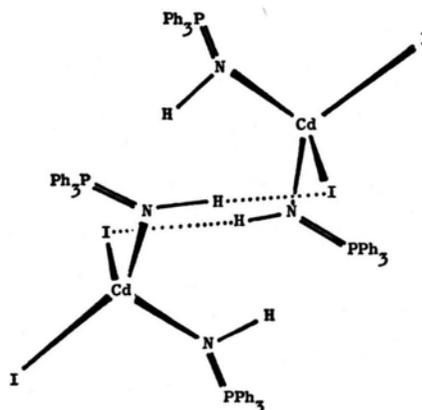
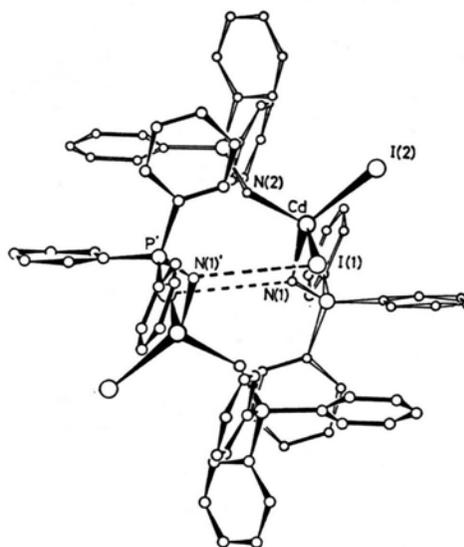
A number of metal complexes of triphenylphosphinimine [1-3], N-arylphosphinimine [4], and the triphenylphosphinimidato anion [5, 6] have been reported in recent years. These ligands have been observed in situations where they are formally one [5, 6], two [4] and four electron [3] donors, and further the N-aryltriphenylphosphinimines have been shown to be valuable precursors for the formation of metal organo-nitrene complexes [7].

As part of a wider investigation of the coordination chemistry of phosphinimines, and the iso-electronic ylids; we have prepared a number of triphenylphosphinimine complexes, and we note herein the novel features of the cadmium iodide complex. Solutions of cadmium iodide and triphenylphosphinimine in ethanol underwent reaction to produce a white precipitate, which was recrystallized from chloroform to produce a complex of stoichiometry (Ph<sub>3</sub>P:NH)<sub>2</sub>CdI<sub>2</sub> · CHCl<sub>3</sub>.

Crystal data: [CdI<sub>2</sub>(HN:PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> · 2 CHCl<sub>3</sub>, triclinic,  $a = 15.202 \pm 0.003$ ,  $b = 12.916 \pm 0.002$ ,  $c = 13.111 \pm 0.002$  Å,  $\alpha = 99.55^\circ \pm 0.01$ ,  $\beta = 124.64^\circ \pm 0.02$ ,  $\gamma = 100.86^\circ \pm 0.01$ , space group  $P\bar{1}$ ,  $Z = 1$ ,  $D_c = 1.764$  g cm<sup>-3</sup>, CuK $\alpha$ ,  $\lambda = 1.54051$  Å, four circle diffractometry, 1454 independent reflections with  $I > 3\sigma(I)$ .

The conventional  $R$  is 0.09 with anisotropic temperature factors on the heavy atoms and isotropic factors on all other atoms except hydrogen, which were not located.

The molecule contains two [CdI<sub>2</sub>(HN:PPh<sub>3</sub>)<sub>2</sub>] units, with nitrogen and iodine co-ordinated to each cadmium in an approximately tetrahedral arrangement. Whilst the Cd-N distances are equivalent (2.19(2) and 2.17(2) Å), the two Cd-I distances are different (Cd-I(1) 2.773(8) and Cd-I(2) 2.735(6) Å). Further, the iodine with the longer Cd-I bond forms a short contact (3.76(1) Å) to nitrogen atom N(1)'



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in a second unit, which is related to the first by the centre of symmetry.

The  $P-N(1) \cdots I(1)$  angle is  $122^\circ$ , and there are two distinct N-H stretching frequencies in the infrared spectrum (300 K) at  $3338$  and  $3259 \text{ cm}^{-1}$ . In the cubic CsCl structure (266 K) of  $\text{NH}_4\text{I}$ , the  $I \cdots N$  distance [8] is  $3.78 \text{ \AA}$ . Here the N-H bonds are believed to be directed towards four of the eight corners of the unit cell [9-11], with the choice of the group of four corners being random from cell to

cell, thus the  $3.78 \text{ \AA}$  distance quoted is the mean between  $N(H) \cdots I$  and  $(H)N \cdots I$ .

It does seem likely therefore that the  $N \cdots I$  contact of  $3.76 \text{ \AA}$  in  $[\text{CdI}_2(\text{NH}:\text{PPh}_3)_2]_2$  represents an  $N-H \cdots I$  hydrogen bond, and that the molecule can be described as a hydrogen-bonded eight membered ring cyclic-dimer, as illustrated in the figure.

Full details concerning the crystallographic part of this work can be obtained from the authors.

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