

# A copper(I) coordination polymer containing an adamantane P–N cage ligand

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### Key indicators

Single-crystal X-ray study  
 T = 100 K  
 Mean  $\sigma(\text{C}-\text{N}) = 0.003 \text{ \AA}$   
 R factor = 0.027  
 wR factor = 0.069  
 Data-to-parameter ratio = 21.3

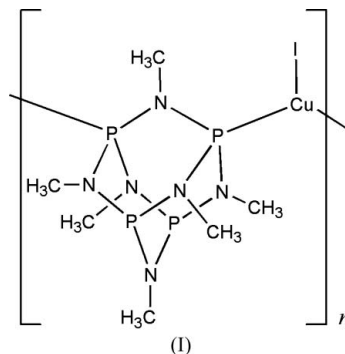
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

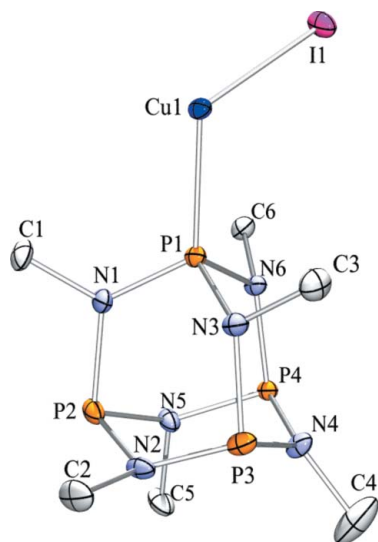
The tetradentate non-chelating ligand 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexaaza-1,3,5,7-tetraphosphaadamantane,  $\text{P}_4(\text{NCH}_3)_6$ , reacts with one equivalent of cuprous iodide to yield the title coordination polymer, *catena*-poly[[iodo-copper(I)]- $\mu$ -2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexaaza-1,3,5,7-tetraphosphaadamantane- $\kappa^2\text{P}^1:\text{P}^3$ ],  $[\text{CuI}(\text{C}_6\text{H}_{18}\text{N}_6\text{P}_4)]_n$ . The polymer is linked through P–Cu coordination at two vertices of the cage. The  $\text{Cu}^{\text{I}}$  ions have a trigonal-planar geometry, coordinated by P atoms from two different ligands and the iodide. This structure represents the first crystallographically characterized coordination compound of this cage ligand.

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### Comment

Spectroscopic studies have shown that the cage compound  $\text{P}_4(\text{NCH}_3)_6$  can coordinate up to four Lewis acids [ $\text{Ni}(\text{CO})_3$ , or  $\text{BH}_3$ ], one at each P vertex (Reiss & Van Wazer, 1967, 1968). Crystallographic studies of chalcogenide derivatives  $\text{P}_4(\text{NCH}_3)_6\text{X}_n$  ( $\text{X} = \text{O}$  or  $\text{S}$ ,  $n = 1-4$ ) have also been reported (Casabianca *et al.*, 1978; Cotton *et al.*, 1982, 1983). To date, no crystallographic characterization has been carried out on the coordination complexes of  $\text{P}_4(\text{NCH}_3)_6$ . We have found this ligand to be effective at coordinating soft metal ions and here report the crystal structure of the coordination polymer  $[\text{P}_4(\text{NCH}_3)_6\text{CuI}]_n$ , (I). The Cu–P bond lengths are consistent with other known structures of  $\text{Cu}^{\text{I}}$  with P–N ligands at 2.2434 (8) and 2.2390 (8) Å for Cu1–P1 and Cu1–P4<sup>1</sup>, respectively [symmetry code: (i)  $2 - x, y + \frac{1}{2}, -z + \frac{1}{2}$ ]. IR spectroscopy of solid (I) as a KBr pellet indicated a shift in  $\nu(\text{P}-\text{N})$  from  $825 \text{ cm}^{-1}$  for the uncomplexed ligand to  $853 \text{ cm}^{-1}$ , with shoulders at  $871$  and  $880 \text{ cm}^{-1}$ , for the complexed ligand. This shift is consistent with previous studies of the chalcogenide derivatives of the ligand (Casabianca *et al.*, 1977).





**Figure 1**  
Displacement ellipsoid plot of the monomer unit. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

monomeric analog of  $P_4(NCH_3)_6$ . The HMPT complex of  $Cu^I$  forms a cube-shaped  $Cu_4I_4$  core with the P ligands bound peripherally to the four Cu vertices (Arkhireeva *et al.*, 1990). The crystallographic cone angle for the cage ligand is estimated to be  $140^\circ$ , roughly  $10^\circ$  larger than that of HMPT (Mueller & Mingos, 1995).

The internal structure of the cage shows minor distortions to the P–N bond lengths typical of this family of compounds (Cotton *et al.*, 1978, 1982, 1983). The bond lengths for P atoms bonded to Cu (P1 and P4) are consistently shorter than those for non-coordinated P atoms. The geometry around the N atoms in the cage is roughly planar. The sum of angles around N atoms ranges from  $356$  to  $346^\circ$ . The least planar N atoms are at positions where this distortion relieves crowding between methyl groups of neighboring cages. The P...P distances within the cage range from  $2.975$  to  $3.037$  Å.

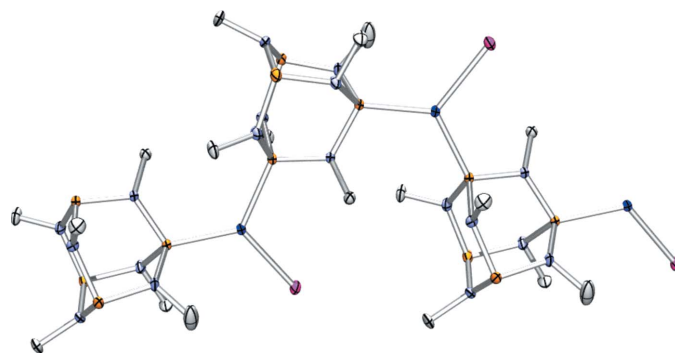
## Experimental

Manipulations were carried out using standard Schlenk techniques. The title compound was prepared by cannula addition of cuprous iodide (0.050 g) in freshly distilled acetonitrile (20 ml) to a similarly prepared solution of  $P_4(NCH_3)_6$  (0.105 g). Some precipitation occurred immediately. The reaction flask was sealed under nitrogen and refrigerated at 277 K. Crystal formation was observed after two days. The white blocks are air stable over a period of one week.

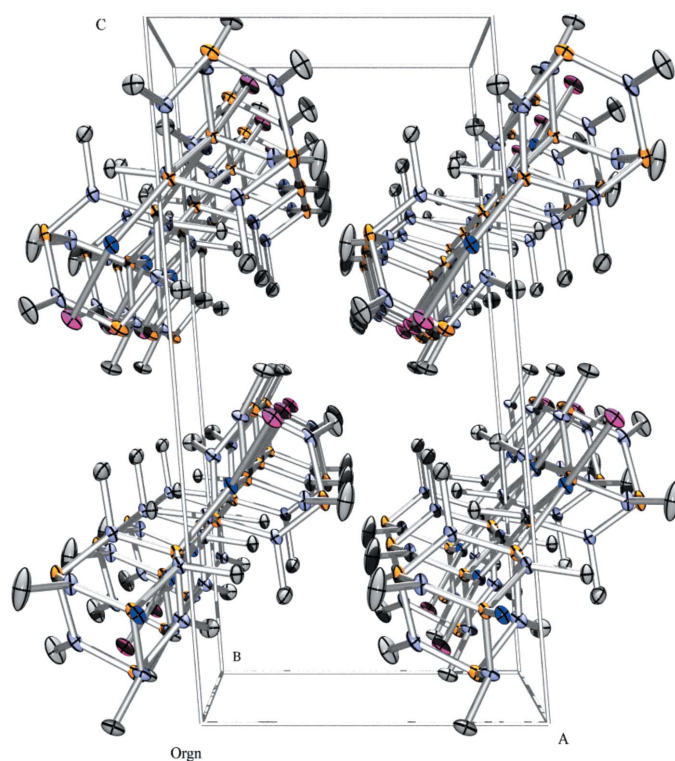
### Crystal data

$[CuI(C_6H_{18}N_6P_4)]$   
 $M_r = 488.58$   
Monoclinic,  $P2_1/c$   
 $a = 8.4321$  (5) Å  
 $b = 11.6068$  (7) Å  
 $c = 16.2351$  (10) Å  
 $\beta = 94.863$  (1) $^\circ$   
 $V = 1583.20$  (17) Å $^3$   
 $Z = 4$

$D_x = 2.05$  Mg m $^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 6312 reflections  
 $\theta = 2.4$ – $27.5^\circ$   
 $\mu = 3.73$  mm $^{-1}$   
 $T = 100$  (2) K  
Block, colorless  
 $0.19 \times 0.16 \times 0.14$  mm



**Figure 2**  
Displacement ellipsoid plot of  $[P_4(NCH_3)_6CuI]_n$  ( $n = 3$ ). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.



**Figure 3**  
View along the  $b$  axis of  $P_4(NCH_3)_6CuI_n$ . Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.474$ ,  $T_{max} = 0.594$   
9801 measured reflections

3605 independent reflections  
3234 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.022$   
 $\theta_{max} = 27.5^\circ$   
 $h = -10 \rightarrow 8$   
 $k = -14 \rightarrow 15$   
 $l = -21 \rightarrow 20$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.069$   
 $S = 1.03$   
3605 reflections  
169 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 1.8652P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 1.23$  e Å $^{-3}$   
 $\Delta\rho_{min} = -0.71$  e Å $^{-3}$

H atoms were placed at appropriate positions ( $C-H = 0.98 \text{ \AA}$ ) and refined with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The largest peak of residual electron density is  $1.02 \text{ \AA}$  from C4. The position of atoms C2 and C4 in a relatively open region of space in the crystal structure allows greater vibrational motion, resulting in elongated displacement ellipsoids for these atoms. Modeling of C4 as a disordered methyl group with refined occupancy gave no improvement in structure refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *POV-Ray* (Persistence of Vision Pty. Ltd, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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