Electronic Supplementary Information

Metalation Studies of 3- and 4-Pyridyloxycyclophosphazenes:

Metallamacrocycles to Coordination Polymers

Vadapalli Chandrasekhar[*] and Ramakirushnan Suriyanarayanan

Department of Chemistry, Indian Institute of Technology, Kanpur, Kanpur 208 016, India

Corresponding Author:
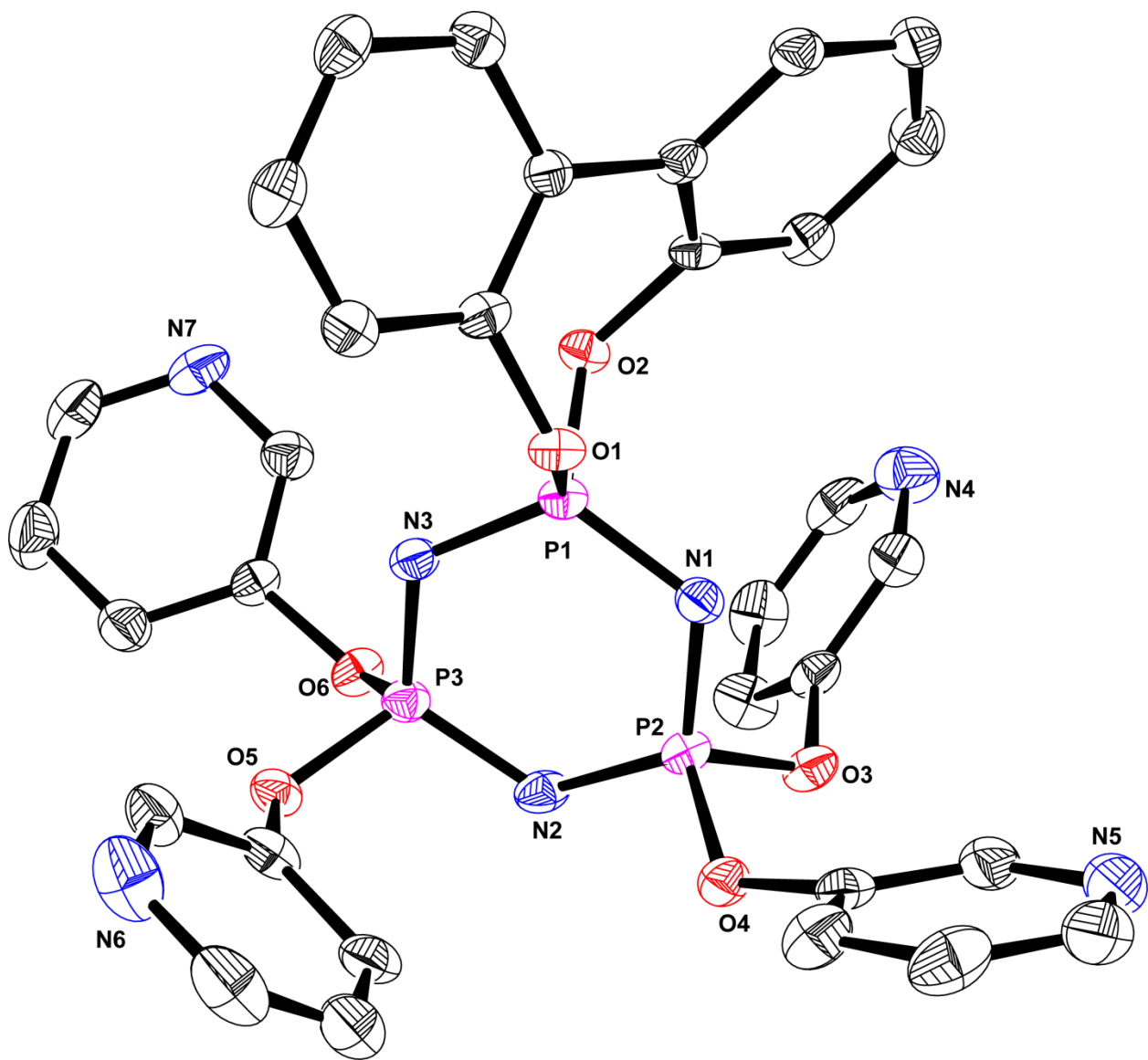Email: vc@iitk.ac.in; Tel: +91 512 259 7259. Fax: +91 512 259 7436.
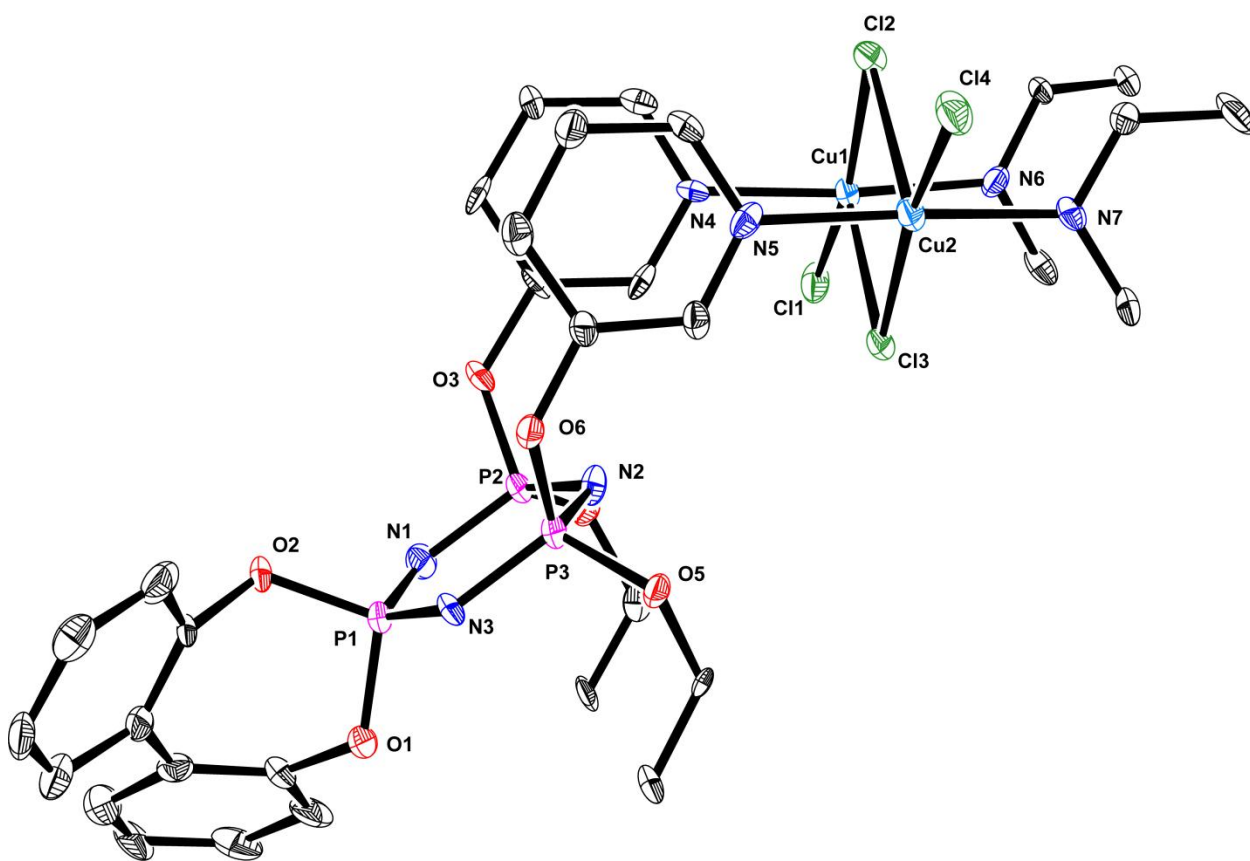
Fig. S1 ORTEP diagram of Ligand L1 (50% probability)

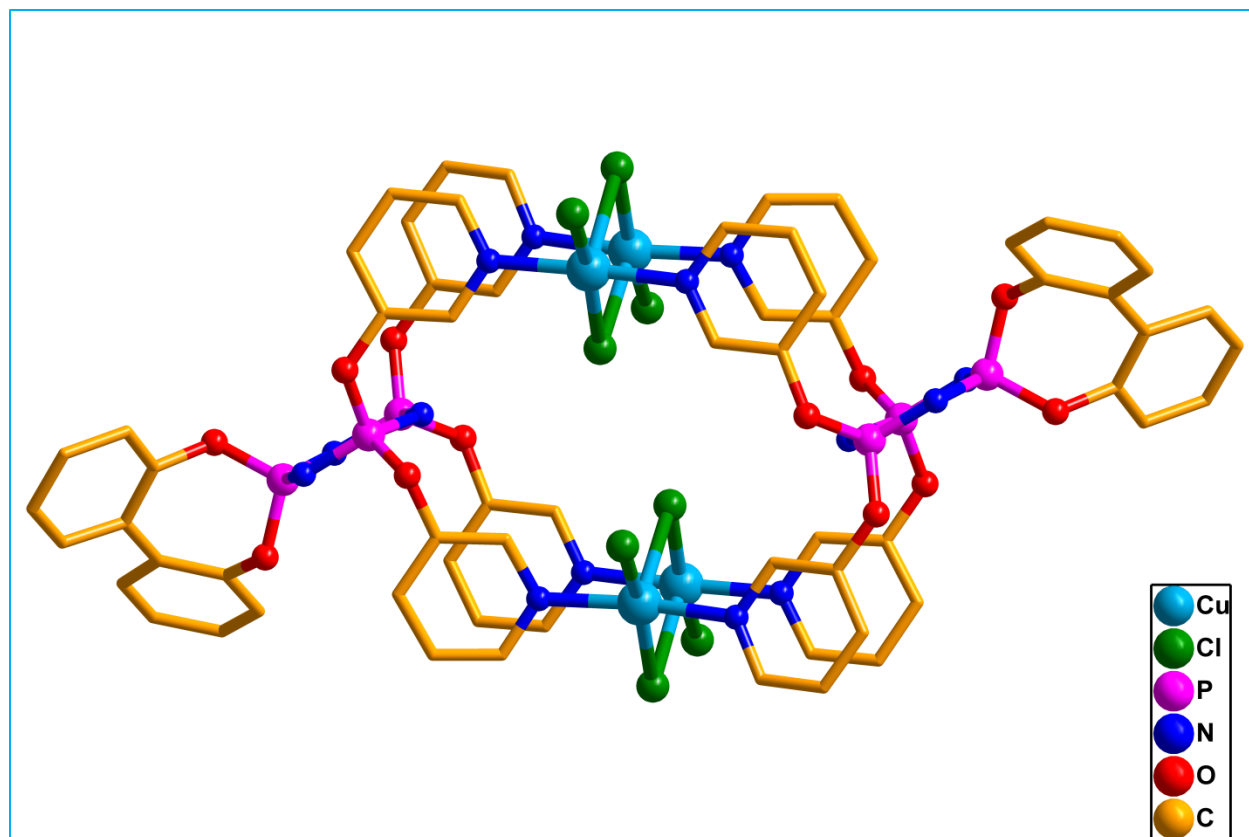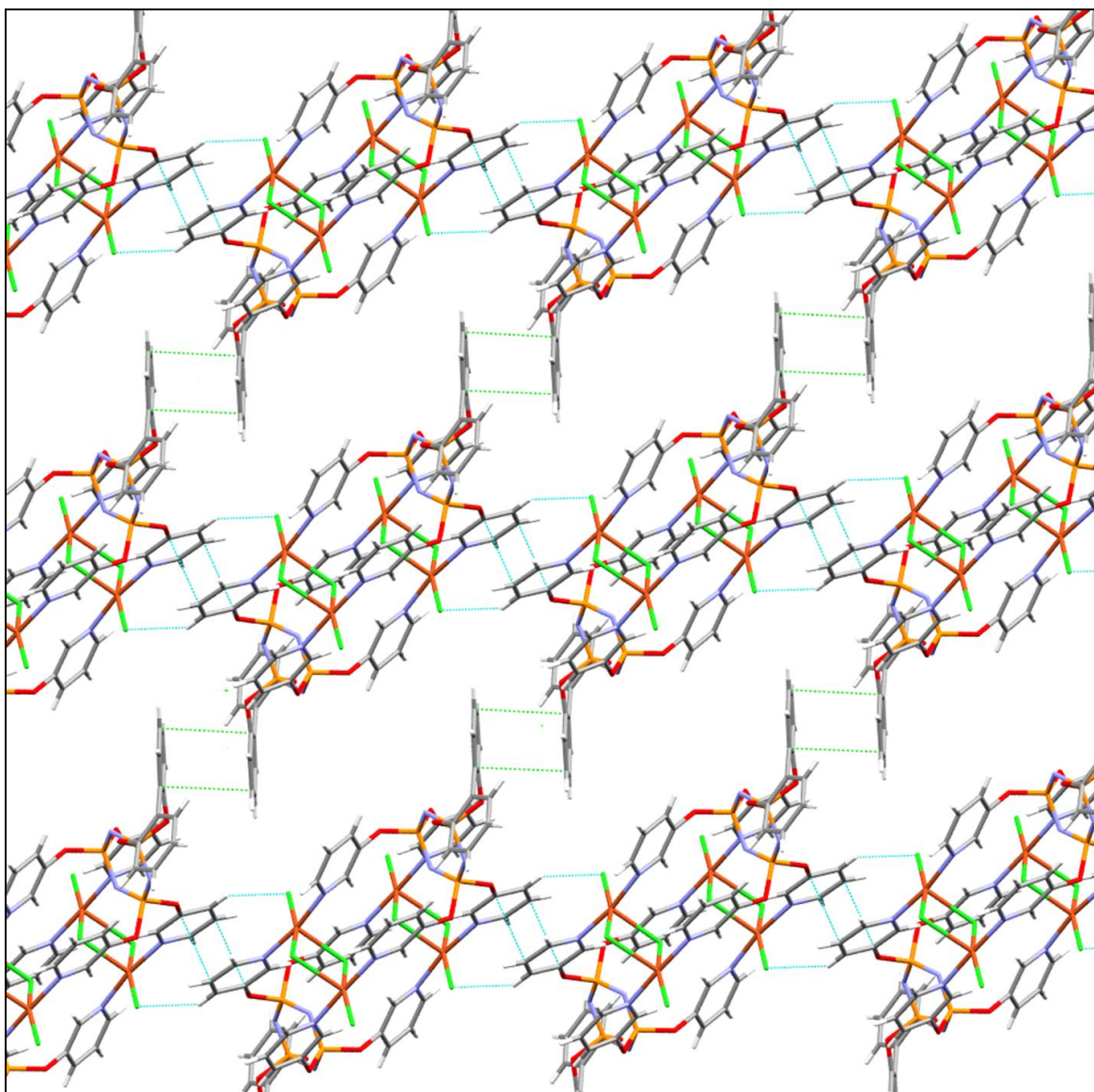Fig. S2 ORTEP diagram of the asymmetric unit of **3**

Fig. S3 Another view of **3**

Fig. S4 2D supramolecular network formation in compound **3** along *b* axis via π-π staking
between 3-oxopyridine rings(3.337 Å) and also biphenyloxy rings(3.83 Å) Diagram also shows
the H…Cl (2.671 Å) interactions between coordinated chlorine atom and hydrogen atom of 3-
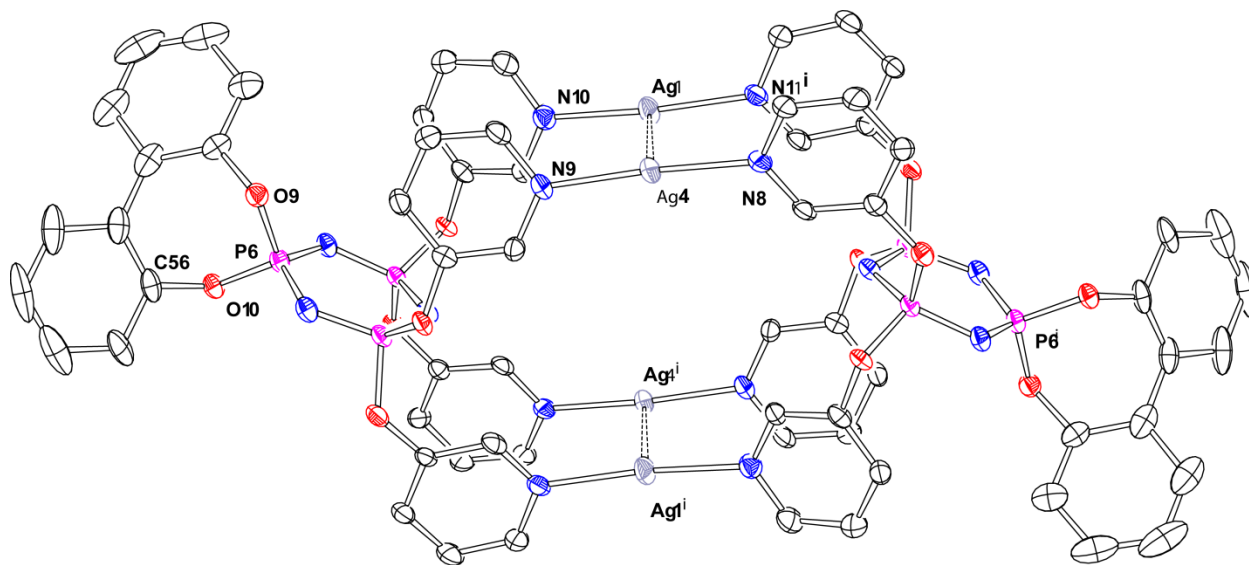oxopyridine units

Fig. S5 ORTEP diagram of **4**. Anions, solvent and hydrogen atoms have been omitted for clarity.
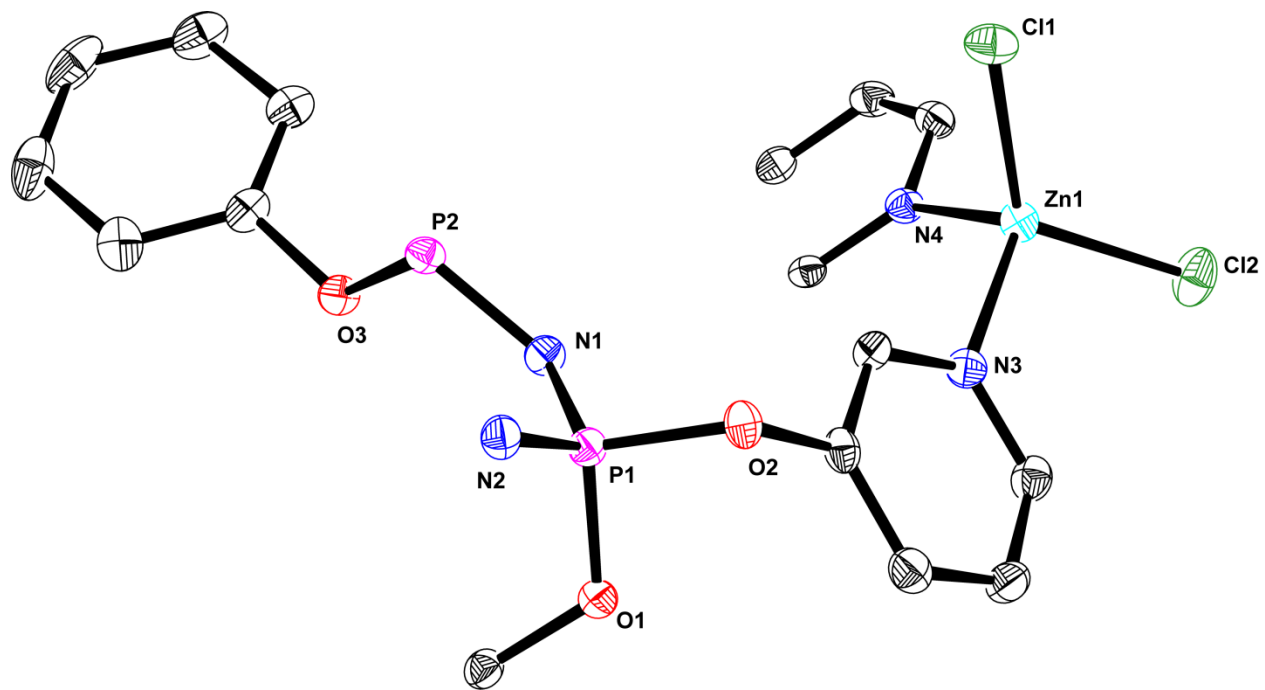
Fig. S6 ORTEP diagram showing the asymmetric unit of **5** (solvent molecules have been omitted for clarity)

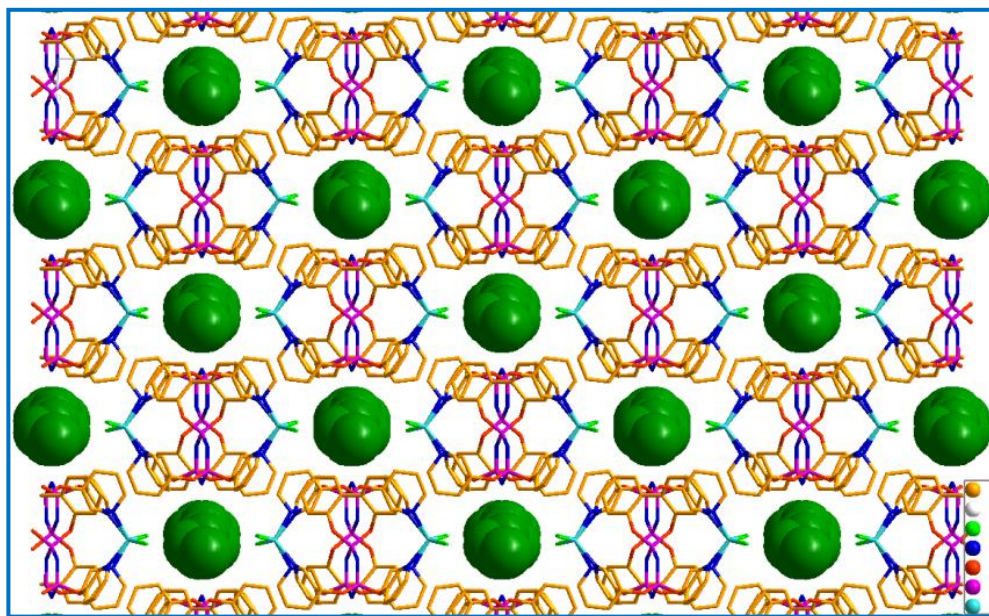Fig. S7 Molecular packing view of **5** along crystallographic *c* axis (hydrogen atoms have been omitted for clarity; disordered MeOH molecules are shown as a green colored space filling model)
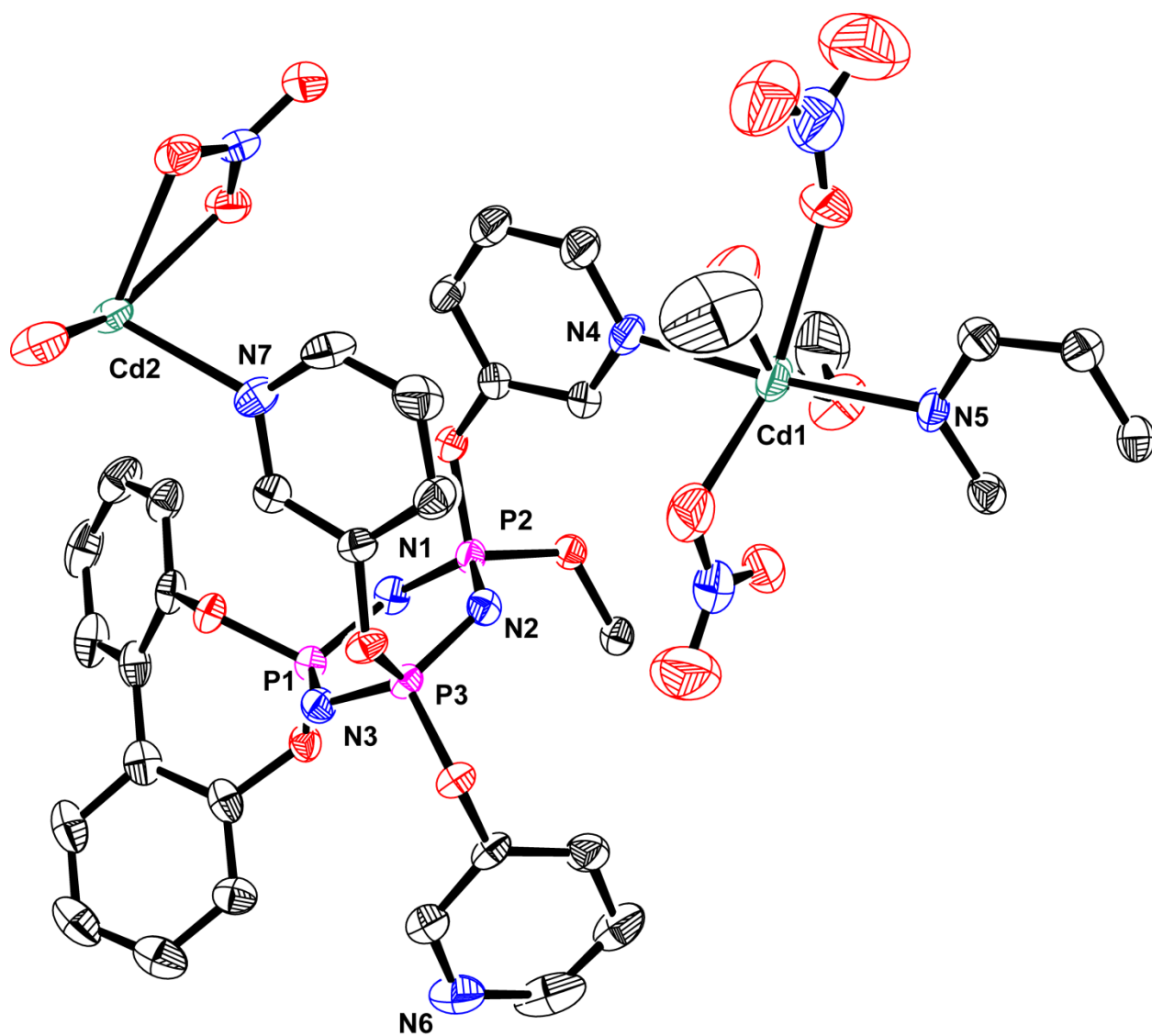
Fig. S8 ORTEP diagram showing the asymmetric unit of **6**
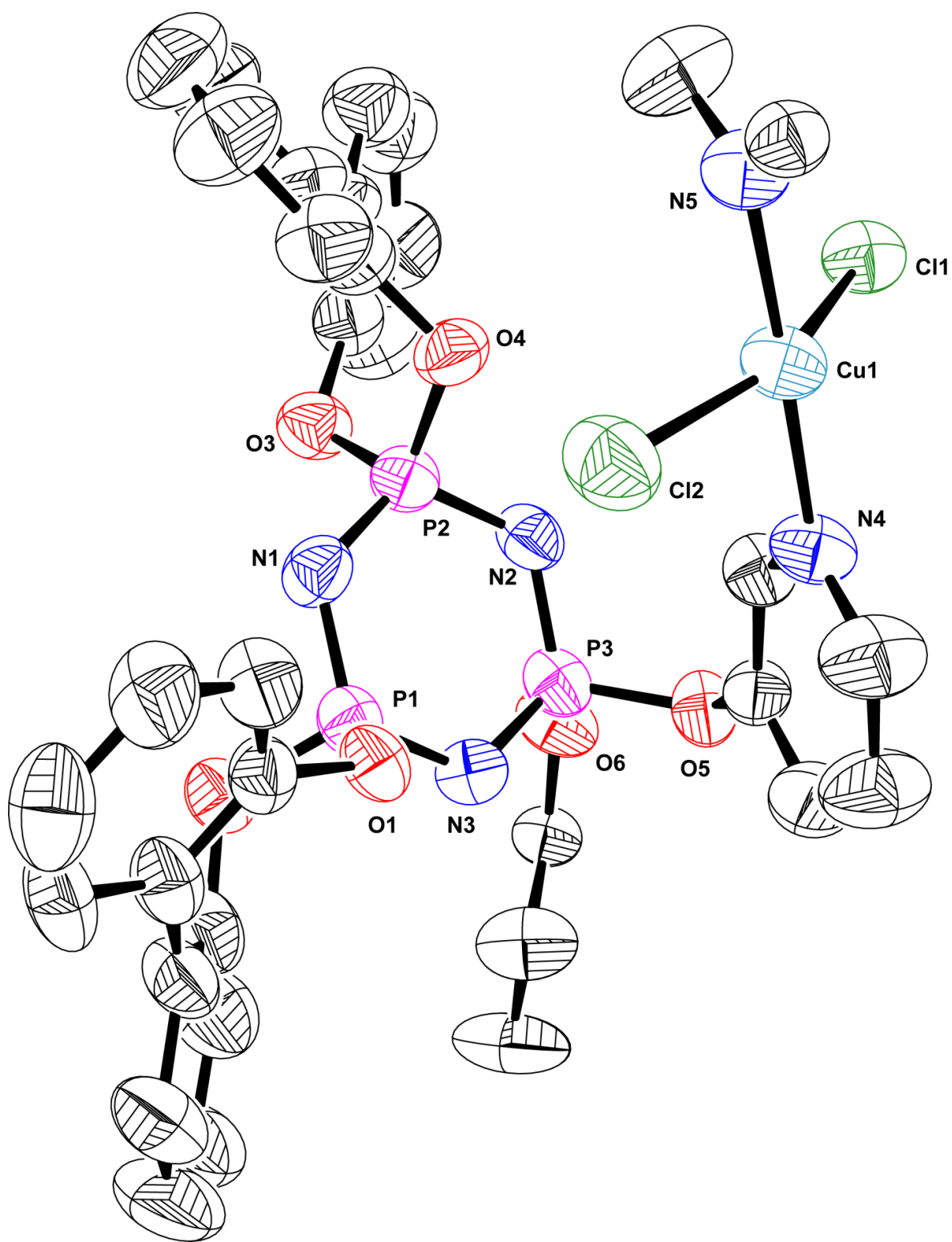
Fig. S9 ORTEP diagram of **8**
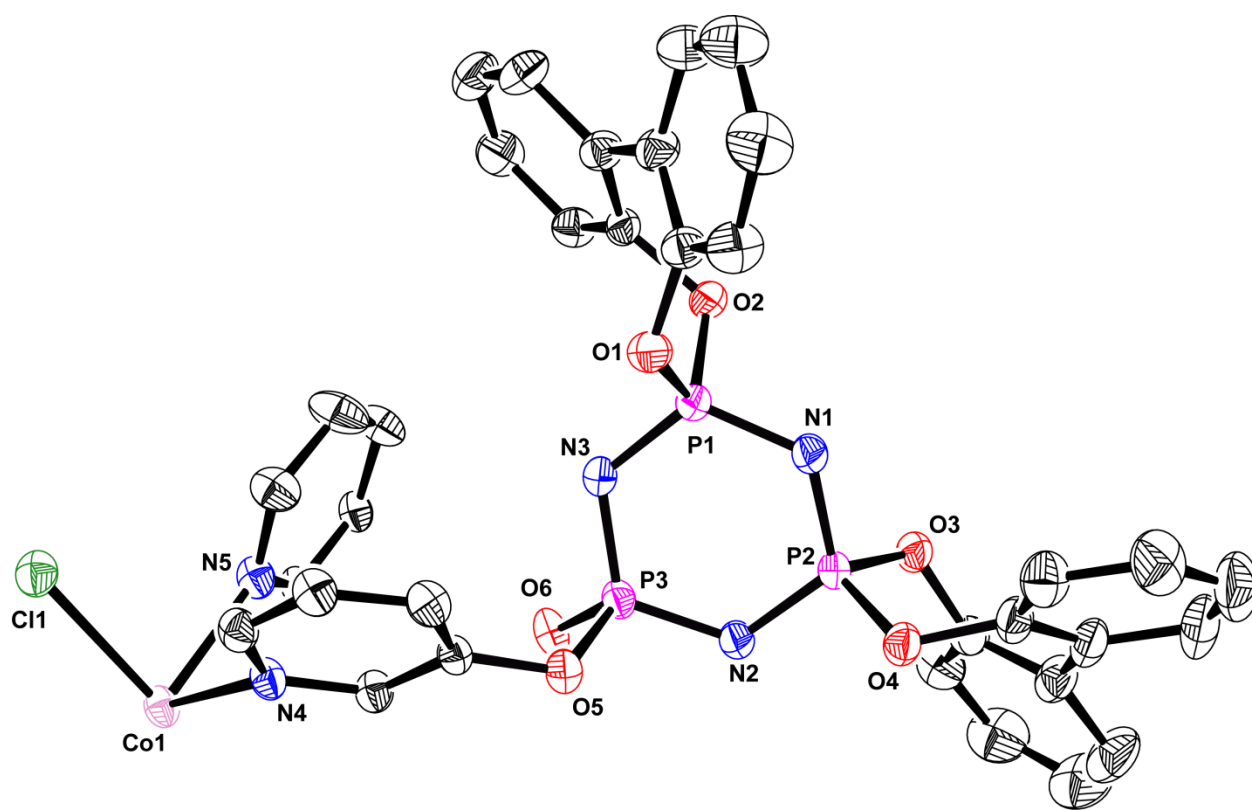
Fig. S10 ORTEP diagram of the asymmetric unit of **7**
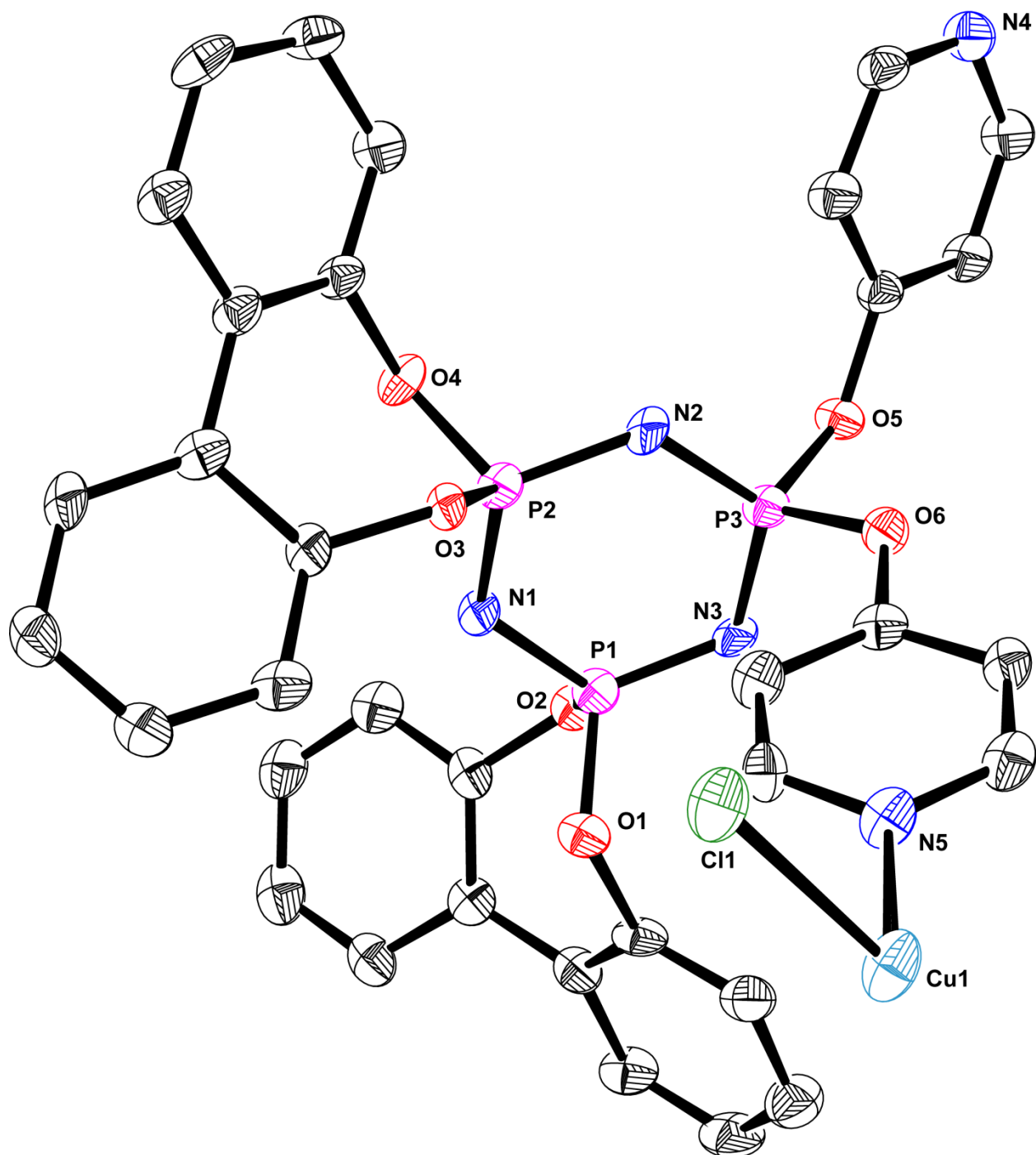
Fig. S11 ORTEP diagram of the asymmetric unit of **9**

	C
	Cl
	Cu
	N
	O
	P
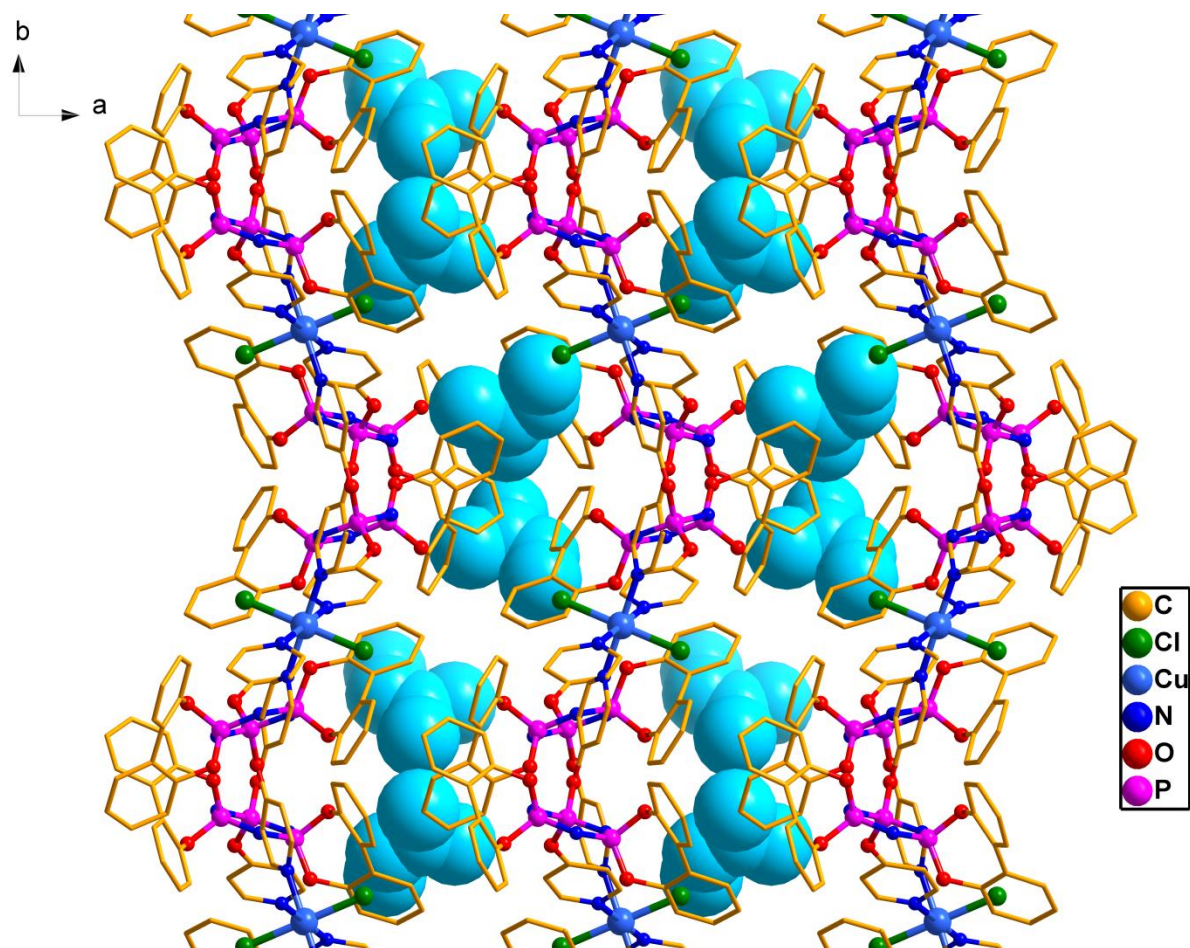
Fig. S12 Packing diagram of **9** in the crystallographic 'c' axis. DMF molecules (space filling model) occupy the space between two layers of (4, 4) 2D nets of **9**
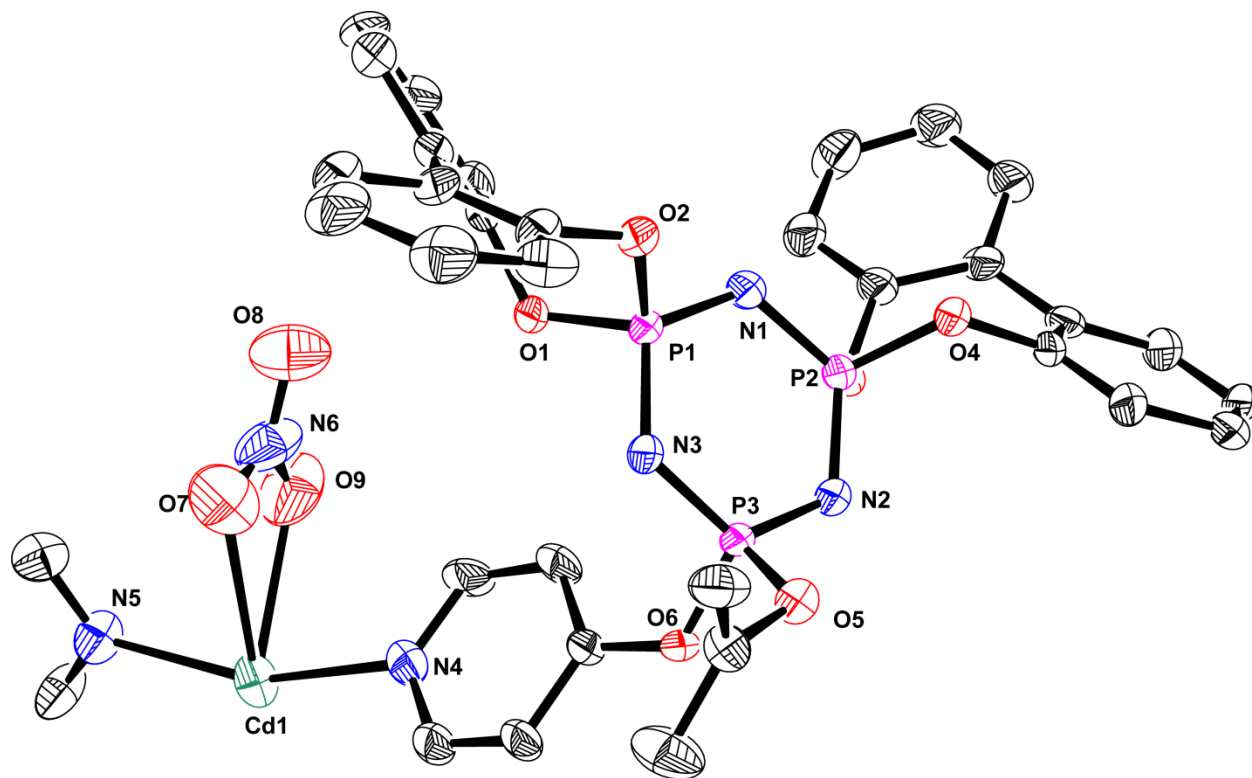
Fig. S13 ORTEP diagram of asymmetric unit of **10**

Fig. S14 Thermogravimetric analysis curves for compounds **L2, 7, 8**

Fig. S15 Thermogravimetric analysis curves for compounds **L3, 9, 10**

Fig. S16 EPR spectrum of **9** in DMF-toluene glass at -120 °C

Fig. S17 A view of the square antiprismatic Cd(II) center in the compound **10**

Table S1 P-N and P-O bond distances and P-N-P and N-P-N bond angles for compounds **L1**, **3-6**

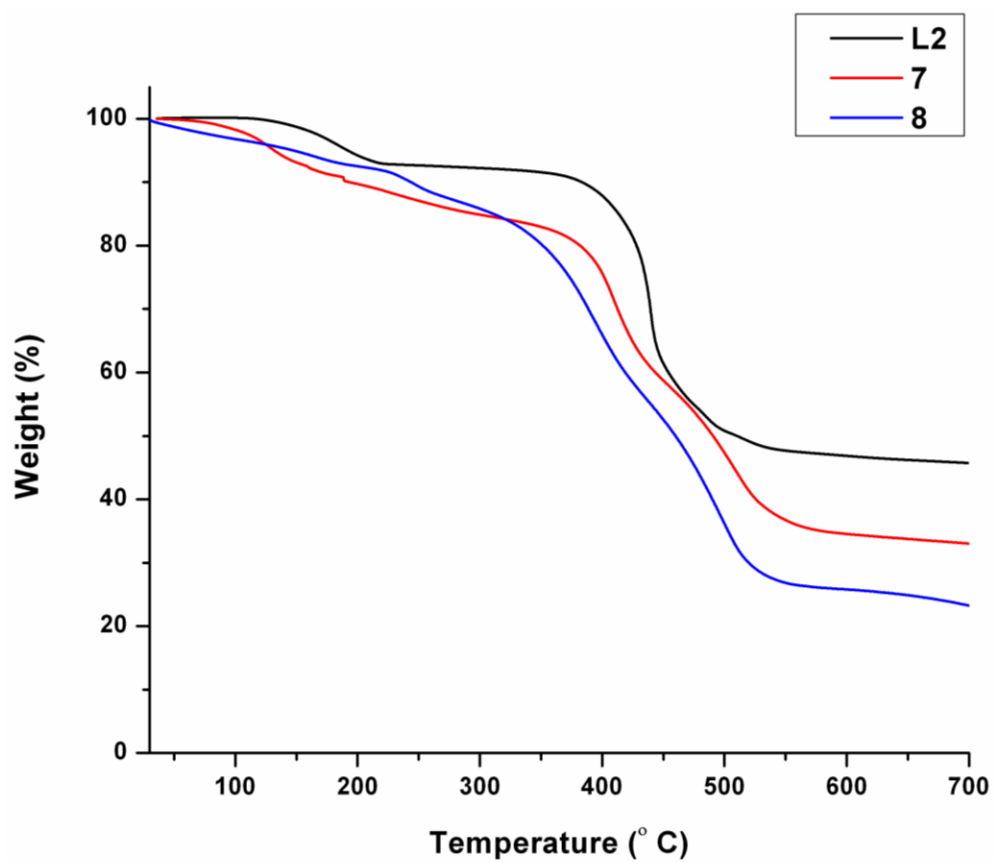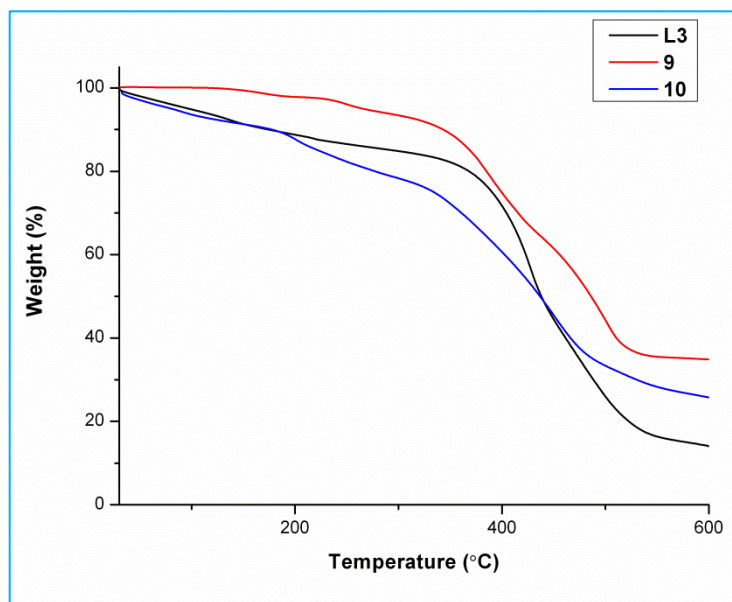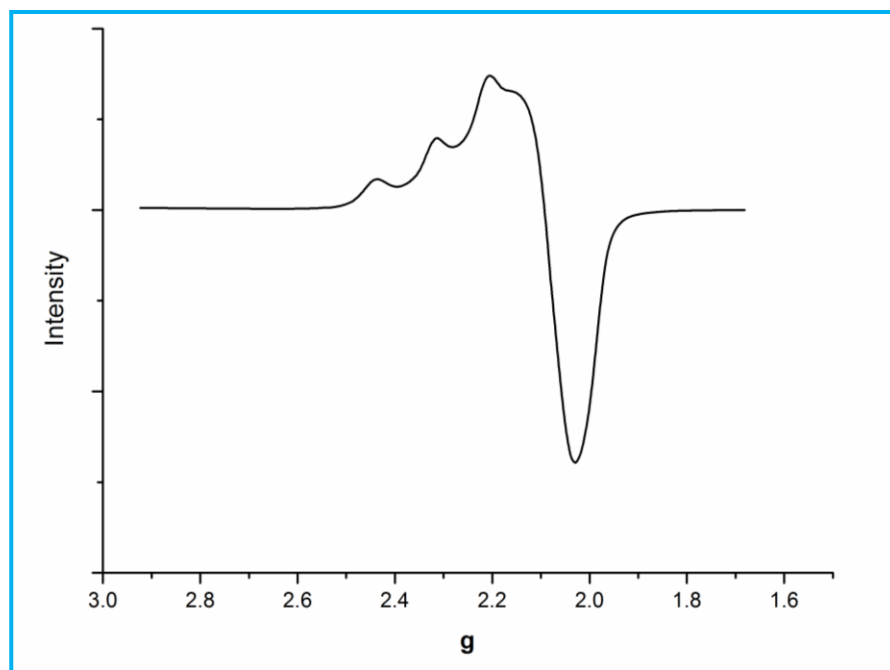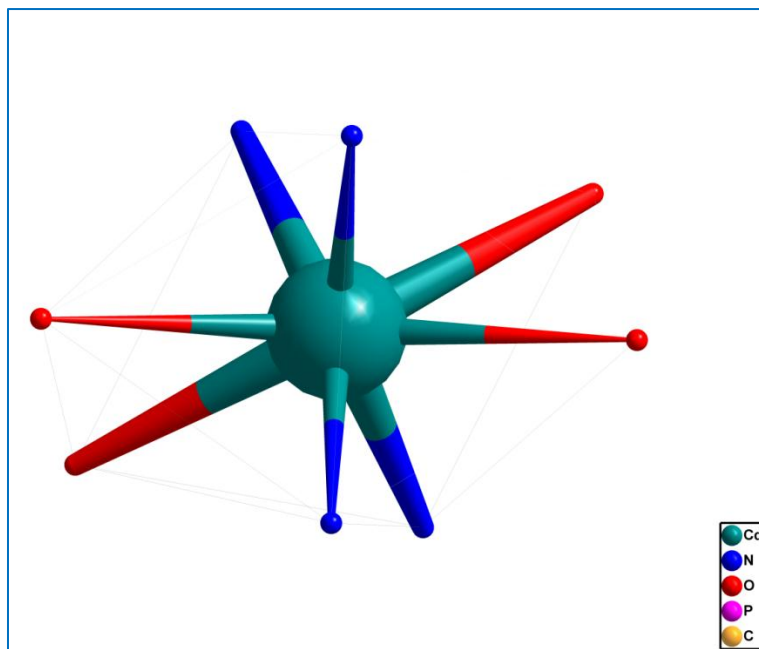| Compound	P-N and P-O bond distance (Å)		P-N-P and N-P-N bond angle (°)
L1	P(1)-N(1) 1.575(4)	P(1)-O(1) 1.589(3)	N(1)-P(1)-N(3) 117.39(16)
	P(1)-N(3) 1.592(4)	P(1)-O(2) 1.600(3)	N(1)-P(2)-N(2) 118.18(15)
	P(2)-N(1) 1.576(4)	P(2)-O(3) 1.580(3)	N(3)-P(3)-N(2) 118.02(15)
	P(2)-N(2) 1.580(4)	P(2)-O(4) 1.591(3)	P(1)-N(1)-P(2) 122.13(18)
	P(3)-N(2) 1.575(4)	P(3)-O(5) 1.585(3)	P(2)-N(2)-P(3) 121.67(19)
	P(3)-N(3) 1.581(4)	P(3)-O(6) 1.588(3)	P(3)-N(3)-P(1) 122.14(18)
3	P(1)-N(1) 1.567(5)	P(1)-O(1) 1.584(4)	N(1)-P(1)-N(3) 118.1(2)
	P(1)-N(3) 1.573(5)	P(1)-O(2) 1.590(4)	N(1)-P(2)-N(2) 117.4(3)
	P(2)-N(1) 1.576(5)	P(2)-O(3) 1.593(4)	N(3)-P(3)-N(2) 117.3(3)
	P(2)-N(2) 1.584(5)	P(2)-O(4) 1.587(4)	P(1)-N(1)-P(2) 121.8(3)
	P(3)-N(2) 1.576(5)	P(3)-O(5) 1.592(4)	P(2)-N(2)-P(3) 121.0(3)
	P(3)-N(3) 1.583(5)	P(3)-O(6) 1.574(4)	P(3)-N(3)-P(1) 121.5(3)
4	P(1)-N(1) 1.562(4)	P(1)-O(1) 1.584(3)	N(1)-P(1)-N(3) 117.63(2)
	P(1)-N(3) 1.588(3)	P(1)-O(2) 1.583(3)	N(1)-P(2)-N(2) 118.17(2)
	P(2)-N(1) 1.583(3)	P(2)-O(3) 1.587(3)	N(3)-P(3)-N(2) 118.05(2)
	P(2)-N(2) 1.586(3)	P(2)-O(4) 1.596(3)	P(1)-N(1)-P(2) 122.0(2)
	P(3)-N(2) 1.563(3)	P(3)-O(5) 1.581(3)	P(2)-N(2)-P(3) 120.2(2)
	P(3)-N(3) 1.583(3)	P(3)-O(6) 1.590(3)	P(3)-N(3)-P(1) 121.3(2)
5	P(1)-N(1)[#1] 1.583(4)	P(1)-O(1)[#1] 1.584(4)	N(1)[#1]-P(1)-N(1) 117.8(3)
	P(1)-N(1) 1.583(4)	P(1)-O(1) 1.585(4)	N(2)-P(2)-N(1) 118.0(3)
	P(2)-N(2) 1.574(3)	P(2)-O(2) 1.582(4)	P(2)-N(1)-P(1) 122.0(3)
	P(2)-N(1) 1.581(4)	P(2)-O(3) 1.593(4)	P(2)[#1]-N(2)-P(2) 122.3(4)
	N(2)-P(2)[#1] 1.574(3)		
6	P(1)-N(1) 1.570(5)	O(1)-P(1) 1.585(4)	N(1)-P(1)-N(3) 117.2(3)
	P(1)-N(3) 1.576(5)	O(2)-P(1) 1.579(4)	N(1)-P(2)-N(2) 115.5(3)
	P(2)-N(1) 1.575(5)	O(3)-P(2) 1.582(4)	N(3)-P(3)-N(2) 118.0(3)
	P(2)-N(2) 1.578(5)	O(4)-P(2) 1.583(4)	P(1)-N(1)-P(2) 123.5(3)
	P(3)-N(2) 1.572(5)	O(5)-P(3) 1.590(4)	P(2)-N(2)-P(3) 122.0(3)
	P(3)-N(3) 1.580(5)	O(6)-P(3) 1.591(5)	P(3)-N(3)-P(1) 120.2(3)

(a)Symmetry transformations used to generate equivalent atoms: #1 1 -x, -y, 1-z

Table S2 Mean plane data for compounds **L1**, **3-6**

Atoms	Distances from the mean plane (Å)				
	L1	**3**	**4**	**5**	**6**
P(1)	0.0055	-0.0144	0.0262	-0.0006	-0.0019
P(2)	0.0019	0.0129	-0.0096	0	0.0015
P(3)	-0.0090	0.0028	0.0060	0.0006 (P2*)	-0.0140
N(1)	-0.0720	0.1572	-0.0659	0.0073	-0.0576
N(2)	0.0598	0.0639	-0.1795	0	-0.0879
N(3)	0.0258	0.0489	0.0818	-0.0073 (N1*)	0.1276

Table S3 P-N and P-O bond distances and P-N-P and N-P-N bond angles for compounds **7** and 8

Compound	P-N and P-O bond distance (Å)		P-N-P and N-P-N bond angle (°)
7	P(1)-N(1) 1.571(3)	P(1)-O(1) 1.581(3)	N(1)-P(1)-N(3) 118.23(17)
	P(1)-N(3) 1.574(3)	P(1)-O(2) 1.590(3)	N(2)-P(2)-N(1) 117.60(16)
	P(2)-N(1) 1.580(3)	P(2)-O(4) 1.580(3)	N(3)-P(3)-N(2) 117.68(16)
	P(2)-N(2) 1.572(3)	P(2)-O(3) 1.581(3)	P(1)-N(1)-P(2) 120.43(19)
	P(3)-N(2) 1.587(3)	P(3)-O(5) 1.576(3)	P(2)-N(2)-P(3) 121.87(19)
	P(3)-N(3) 1.571(3)	P(3)-O(6) 1.578(3)	P(3)-N(3)-P(1) 120.61(19)
8	P(1)-N(1) 1.564(7)	P(1)-O(1) 1.570(6)	N(1)-P(1)-N(3) 117.7(3)
	P(1)-N(3) 1.577(7)	P(1)-O(2) 1.582(5)	N(1)-P(2)-N(2) 117.1(3)
	P(2)-N(1) 1.560(7)	P(2)-O(3) 1.570(5)	N(3)-P(3)-N(2) 117.8(3)
	P(2)-N(2) 1.567(6)	P(2)-O(4) 1.582(5)	P(2)-N(1)-P(1) 123.0(4)
	P(3)-N(3) 1.565(7)	P(3)-O(5) 1.579(5)	P(2)-N(2)-P(3) 122.2(4)
	P(3)-N(2) 1.581(6)	P(3)-O(6) 1.594(5)	P(3)-N(3)-P(1) 121.3(4)

Table S4 Mean plane data for compounds **7** and **8**

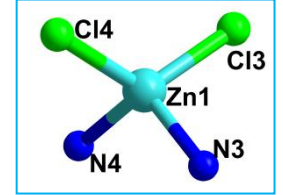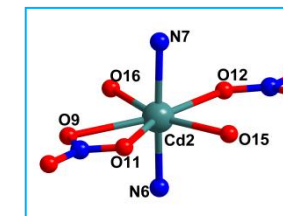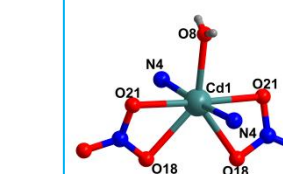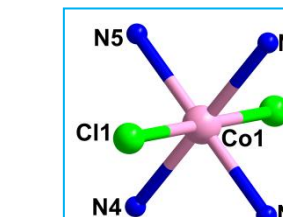| Atoms	Distances from the mean plane (Å)	
	7	**8**
P(1)	0.0288	0.0091
P(2)	-0.0044	-0.0056
P(3)	-0.0094	0.0075
N(1)	-0.1703	0.0031
N(2)	0.1547	0.0312
N(3)	0.1124	-0.1100
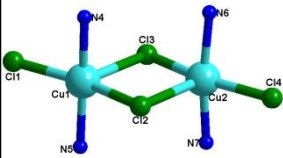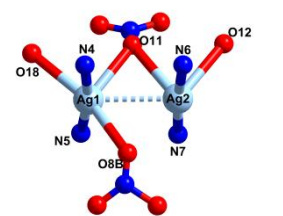
Table S5 P-N and P-O bond distances and P-N-P and N-P-N bond angles for compounds **L3**, **9** and **10**
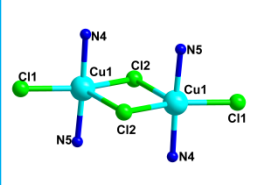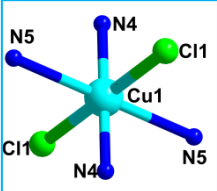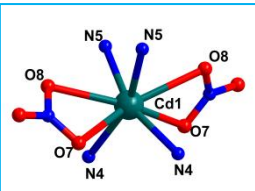
Compound	P-N and P-O bond distance (Å)		P-N-P and N-P-N bond angle (°)
L3[1]	P(1)-N(1) 1.582(7)	P(1)-O(1) 1.584(6)	N(1)-P(1)-N(3) 118.3(4)
	P(1)-N(3) 1.584(7)	P(1)-O(2) 1.601(6)	N(2)-P(2)-N(1) 117.5(4)
	P(2)-N(1) 1.581(7)	P(2)-O(3) 1.575(6)	N(3)-P(3)-N(2) 118.5(4)
	P(2)-N(2) 1.577(7)	P(2)-O(4) 1.588(6)	P(1)-N(1)-P(2) 119.1(4)
	P(3)-N(2) 1.576(7)	P(3)-O(5) 1.572(6)	P(2)-N(2)-P(3) 121.1(4)
	P(3)-N(3) 1.578(7)	P(3)-O(6) 1.588(6)	P(3)-N(3)-P(1) 120.1(4)
9	P(1)-N(1) 1.578(4)	P(1)-O(1) 1.581(3)	N(1)-P(1)-N(3) 118.2(2)
	P(1)-N(3) 1.573(4)	P(1)-O(2) 1.566(3)	N(2)-P(2)-N(1) 117.5(2)
	P(2)-N(1) 1.574(4)	P(2)-O(3) 1.578(3)	N(3)-P(3)-N(2) 117.8(2)
	P(2)-N(2) 1.562(4)	P(2)-O(4) 1.591(3)	P(1)-N(1)-P(2) 121.8(2)
	P(3)-N(2) 1.583(4)	P(3)-O(5) 1.584(3)	P(2)-N(2)-P(3) 122.5(3)
	P(3)-N(3) 1.556(4)	P(3)-O(6) 1.574(3)	P(3)-N(3)-P(1) 122.0(2)
10	P(1)-N(1) 1.577(3)	P(1)-O(1) 1.593(3)	N(1)-P(1)-N(3) 118.73(16)
	P(1)-N(3) 1.574(3)	P(1)-O(2) 1.594(2)	N(1)-P(2)-N(2) 117.46(15)
	P(2)-N(1) 1.572(3)	P(2)-O(3) 1.580(3)	N(3)-P(3)-N(2) 118.53(15)
	P(2)-N(2) 1.582(3)	P(2)-O(4) 1.586(3)	P(2)-N(1)-P(1) 122.16(18)
	P(3)-N(3) 1.580(3)	P(3)-O(5) 1.584(3)	P(2)-N(2)-P(3) 122.08(19)
	P(3)-N(2) 1.576(3)	P(3)-O(6) 1.587(3)	P(3)-N(3)-P(1) 120.94(18)

Table S6 Mean plane data for compounds **L3**, **9** and **10**

Atoms	Distances from the mean plane (Å)		
	L3	**9**	**10**
P(1)	0.0209	-0.0030	0.0015
P(2)	0.0229	0.0058	0.0042
P(3)	-0.0257	0.0034	-0.0026
N(1)	-0.2952	-0.0058	-0.0399
N(2)	0.0724	-0.0698	-0.0030
N(3)	0.0836	0.0149	0.0152

Table S7 Coordination geometry around each metal ion in compounds **3-10**

Compound No.		Geometry, Coordination Environment around metal
3		squarepyramidal, (3Cl, 2N)
4		
5		Tetrahedral (2Cl, 2N)
6		Pentagonalbipyramidal (5O, 2N)
		Pentagonalbipyramidal (5O, 2N)
7		Octahedral, (4N, 2Cl)

8		squarepyramidal, (3Cl, 2N)
9		Octahedral, (4N, 2Cl)
10		Square antiprism, (4N, 4O)

Mask Details[2,3]

Compound **6**

Electron count 337 (void of 3590 Å) per unit cell accounts for 12 MeOH and 12 water molecules (336 total no. of calculated e⁻ (Z=4))

Squeeze Details:

Compound **5**

Electron count 55 (void of 315.6 Å) per unit cell accounts for 0.5(CH_3OH+H_2O) molecules (Z=4)

Compound **8**

Electron count 1091.4(void of 3238 Å) per unit cell accounts for $16CHCl_3$ and 8 methanol molecules (1072 total no. of calculated e⁻ (Z=8))

Compound **10**

Electron count 440 (void of 1249 Å) per unit cell accounts for $8CHCl_3$, CH_2Cl_2 and 8 water molecules (440 total no. of calculated e⁻ (Z=4))

1. Y. Cho, H. Baek and Y. S. Sohn, *Macromolecules*, 1999, **32**, 2167.

2. (a) A. L. Spek, *J.Appl.Cryst.*, 2003, **36**, 3; (b) P. van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194.

3. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339.