The influence of counter ion and ligand methyl substitution on the solid-state structures and photophysical properties of mercury(II) complexes with (E)-N-(pyridin-2-ylmethylene)arylamines†

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ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1 Selected bond lengths, bond angles and torsion angles for optimized structures (B3LYP/6-31G(d,p)) of ligands (L^1-L^4)

Fig. S1 The geometry optimised structure of $\mathbf{L^1}$

Fig. S2 The geometry optimised structure of $\mathbf{L^3}$

Fig. S3 The geometry optimised structure of $\mathbf{L^4}$

Fig. S4 Overlay diagram of [HgI_2L^1] (**3**), illustrated in red, and the inverted molecule of [HgI_2L^4] (**8**), green. The molecules have been aligned to make the five-membered chelate rings coincident.

Fig. S5 Overlay diagram of molecule the Hg1-containing molecule of [$HgBr_2L^4$] (**7**), illustrated in red, and the inverted molecule containing Hg21 of [$HgBr_2L^4$], green. The molecules have been aligned to make the five-membered chelate rings coincident.

Fig. S6 Unit cell contents for **3** viewed in projection down the b-axis. The π...π interactions between the (N1,C1-C5) and $(C7\text{-}C12)^i$ rings are indicated as purple dashed lines [inter-centroid distance = 3.705(2) Å, angle of inclination between the rings = 7.6(2)º for symmetry operation *i*: 1-*x*, 1-*y*, -*z*].

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Fig. S8 Supramolecular layers in the *ac*-plane in **7**. The π...π interactions between the (N1,C1-C5) and $(C27\text{-}C22)^i$, and (C7-C12) and $(N21,C21\text{-}C25)^{ii}$ rings are indicated as purple dashed lines [inter-centroid distances = 3.719(4) and 3.685(4) Å, angles of inclination between the rings = 4.4(3)º and 5.8(3) for symmetry operations *i*: *x*, *y*, 1+*z* and *ii*: 1+*x*, *y*, 1+*z*] and those formed between the chelate ring, $Hg1N_2C_2$, and $(C22\text{-}C27)^i$ [and (C2-C7) and $(Hg2N_2C_2)^i$] shown as blue dashed lines [inter-centroid distances = 3.622(4) and 3.658(4) Å, angle of inclinations = 1.2(3) and 2.5(3)º for *i*: *x*, *y*, 1+*z*. The C5–H5...Br21 [H5...Br21 = 2.85 Å, C5...Br21 = 3.396(7) Å and angle at H5 = 118º] and C25–H25...Br2 [$H25...Br2^{iii}$ = 2.91 Å, $C25...Br2^{iii}$ = 3.767(6) Å and angle at H25 = 151º for *iii*: -1+*x*, *y*, *z*] contacts are shown as orange dashed lines. The

methyl-C–H...π(pyridyl) contacts are shown as brown dashed lines [C13–H13c...Cg(N21,C21-C25)^{i} = 2.85 Å, C13...Cg^{i} = 3.581(8) Å with angle at H13c = 132º; C33–H33a...Cg(N1,C2-C5)^{iv} = 2.83 Å, C33...Cg^{iv} = 3.541(8) Å with angle at H33a = 130º for *iv*: *x*, *y*, -1+*z*].

Fig. S9 View in projection down the *b*-axis of the unit cell contents of **4a**. The π...π interactions between the (N1,C1-C5) and (N1,C1-C5)^{i} [inter-centroid distance = 3.885(6) Å, angle of inclination between the rings = 0º for symmetry operations *i*: 2-*x*, -*y*, 1-*z*], (N21,C21-C25) and (N21,C21-C25)^{ii} [3.549(6) Å, 0º, *ii*: 1-*x*, -*y*, 2-*z*] and (C7-C12) and (C7-C12)^{iii} [3.807(6) Å, 0º, *ii*: 2-*x*, 1-*y*, 2-*z*] are indicated as purple dashed lines. The pyridyl-C–H...Cl contacts are shown as orange dashed lines [C3–H3...Cl1^{i} = 2.83 Å, C3...Cl1^{i} = 3.511(10) Å with angle at H3 = 131º].

Fig. S10 View in projection down the *a*-axis of the unit cell contents of **4b**. The π...π interactions between the (N1,C1-C5) and (N41,C41-C45)^{i} [inter-centroid distance = 3.745(5) Å, angle of inclination between the rings = 5.1(4)º for symmetry operations *i*: 1-*x*, 2-*y*, 1-*z*], (N21,C21-C25) and (N21,C21-C25)^{ii} [3.657(5) Å, 0º, *ii*: 2-*x*, 1-*y*, 1-*z*] and (N61,C61-C65) and (N61,C61-C65)^{iii} [3.760(5) Å, 0º, *ii*: 1-*x*, 1-*y*, 0-*z*] are indicated as purple dashed lines. The pyridyl-C–H...Cl contacts are shown as orange dashed lines [C22–H22...Cl2^{ii} = 2.79 Å, C22...Cl2^{ii} = 3.603(9) Å with angle at H22 = 146º; C45–H45...Cl61 = 2.75 Å, C45...Cl61 = 3.510(8) Å, angle at H45 = 139; C65–H65...Cl41 = 2.75 Å, C65...Cl41 = 3.492(9) Å, angle at H65 = 138].

Fig. S11 View in projection down the *a*-axis of the unit cell contents of **6**. The π...π interactions between the (N1,C1-C5) and (C7-C12)^{i,ii} [inter-centroid distances = 3.808(5) and 3.839(5) Å, angle of inclination between the rings = 13.2(4) and 21.5(4)º for symmetry operations *i*: -1+*x*, *y*, *z* and *ii*: -½+*x*, ½-*y*, ½+*z*] are indicated as purple dashed lines. The pyridyl-C–H...Cl contacts are

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Fig. S12 View in projection down the *a*-axis of the unit cell contents of **10**. The π...π interactions between the (N1,C1-C5) and (C7-C12)^{i} [inter-centroid distance = 3.7808(19) Å, angle of inclination between the rings = 7.83(16)º for symmetry operation *i*: -1-*x*, 1-*y*, -*z*] are indicated as purple dashed lines. The C–H...N contacts are shown as blue dashed lines [C4–H4...N5^{ii} = 2.58 Å, C4...N5^{ii} = 3.268(5) Å with angle at H4 = 129º for *ii*: *x*, *y*, -1+*z*; C6–H6...N8^{iii} = 2.41 Å, C6...N8^{iii} = 3.310(4) Å with angle at H4 = 158º for *iii*: -*x*, 1-*y*, -*z*]. One supramolecular chain has been highlighted in space-filling mode.

Fig. S13 View in projection down the *c*-axis of the unit cell contents of **9**. The C–H...O contacts are shown as orange dashed lines [C2–H2...O5^{i} = 2.49 Å, C4...O5^{i} = 3.346(6) Å with angle at H2 = 150º for *i*: 1-*x*, -½+*y*, ½-*z*; C4–H4...O4^{ii} = 2.60 Å, C4...O4^{ii} = 3.421(6) Å with angle at H4 = 145º for *ii*: -x, -½+y, ½-z; C8–H8...O6^{i} = 2.60 Å, C8...O6^{i} = 3.418(6) Å with angle at H8 = 145º; C9–H9...O1^{iii} = 2.53 Å, C9...O1^{iii} = 3.245(5) Å with angle at H9 = 132º for *iii*: 1+*x*, *y*, *z*; C9–H9...O3^{iv} = 2.53 Å, C9...O3^{iv} = 3.388(5) Å with angle at H9 = 150º for *iv*: 1+*x*, ½-*y*, ½+*z*]. One supramolecular chain has been highlighted in space-filling mode.

Table S1 Selected bond lengths, bond angles and torsion angles for optimized structures (B3LYP/6-31G(d,p)) of ligands (L^1-L^4)[a]

Bond lengths (Å)/ angles (°)	L^1	L^2	L^3	L^4
C1–C2	1.404	1.403	1.404	1.404
C2–C3	1.393	1.393	1.393	1.393
C3–C4	1.392	1.392	1.392	1.392
C4–C5	1.400	1.400	1.400	1.400
C1–C6	1.476	1.477	1.476	1.476
C7–C8	1.409	1.406	1.408	1.408
C8–C9	1.391	1.393	1.390	1.390
C9–C10	1.398	1.395	1.397	1.404
C10–C11	1.395	1.396	1.399	1.400
C11–C12	1.393	1.397	1.398	1.391
C12–C7	1.405	1.415	1.403	1.404
C5–N1	1.332	1.332	1.332	1.332
C1–N1	1.347	1.347	1.347	1.348
C6–N2	1.278	1.277	1.278	1.278
C7–N2	1.409	1.404	1.410	1.408
C5–N1–C1	117.6	117.6	117.6	117.6
C6–N2–C7	122.4	120.3	122.3	122.4
N1–C1–C2	122.4	122.5	122.4	122.3
N1–C1–C6	119.1	118.9	119.1	119.0
C2–C1–C6	118.5	118.6	118.5	118.6
N2–C6–C1	122.6	123.2	122.7	122.6

C12–C7–C8	118.5	119.9	118.7	118.0
C12–C7–N2	115.1	117.6	114.9	115.4
C8–C7–N2	126.4	122.4	126.3	126.6
C5–N1–C1–C6	-179.8	179.9	179.9	180.0
C6–C1–C2–C3	179.8	-179.8	-179.9	-179.9
C7–N2–C6–C1	179.5	-176.9	-179.9	-179.9
C6–N2–C7–C8	0.8	41.3	-0.4	-0.2
C6–N2–C7–C12	-179.0	-142.0	179.8	-179.9

[a] Refer to Figs 1 and S1-S3 for atom numbering schemes

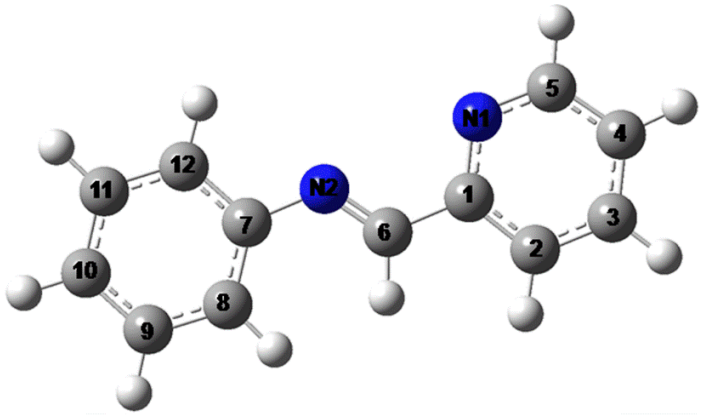


Fig. S1 The geometry optimised structure of $\mathbf{L}^1$

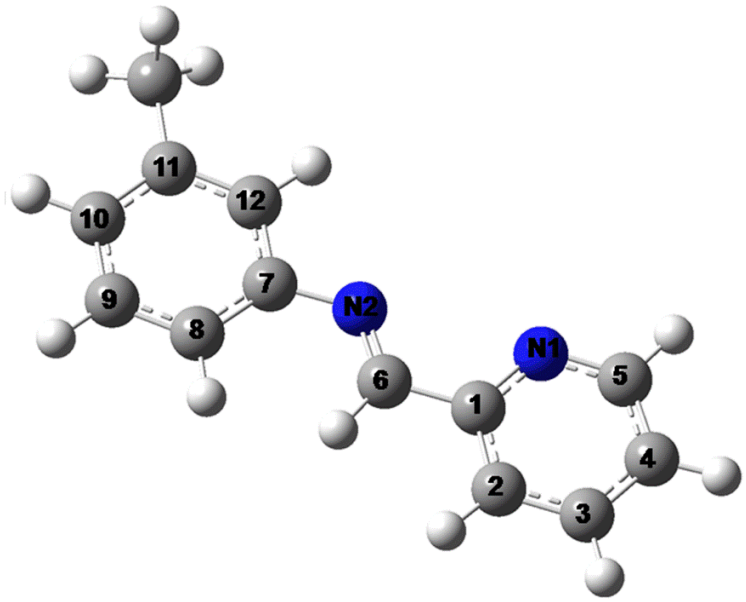


Fig. S2 The geometry optimised structure of $\mathbf{L}^3$

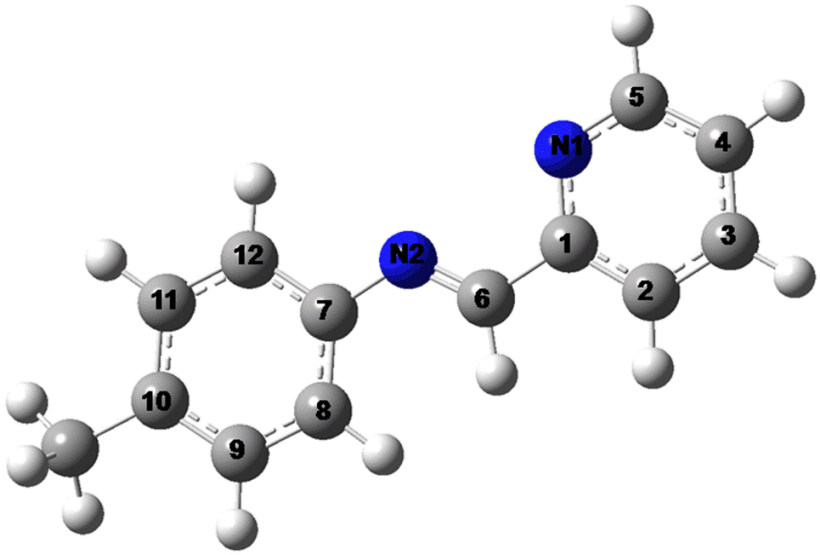
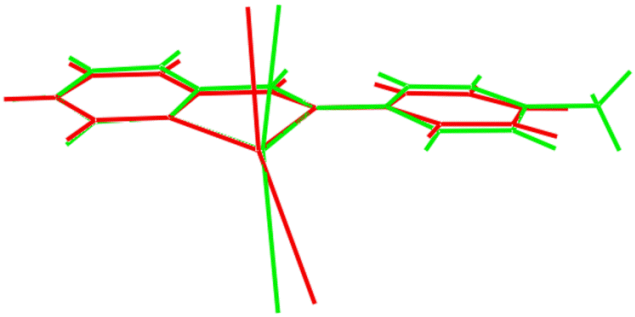


Fig. S3 The geometry optimised structure of $\mathbf{L}^4$



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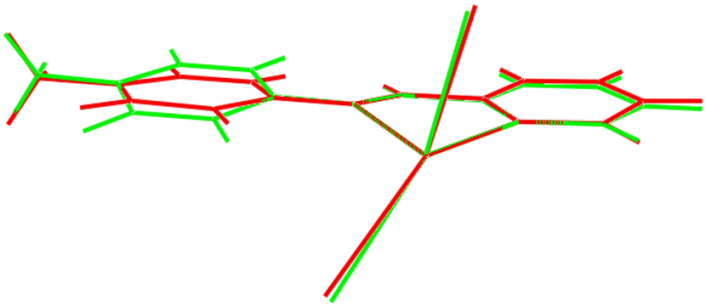

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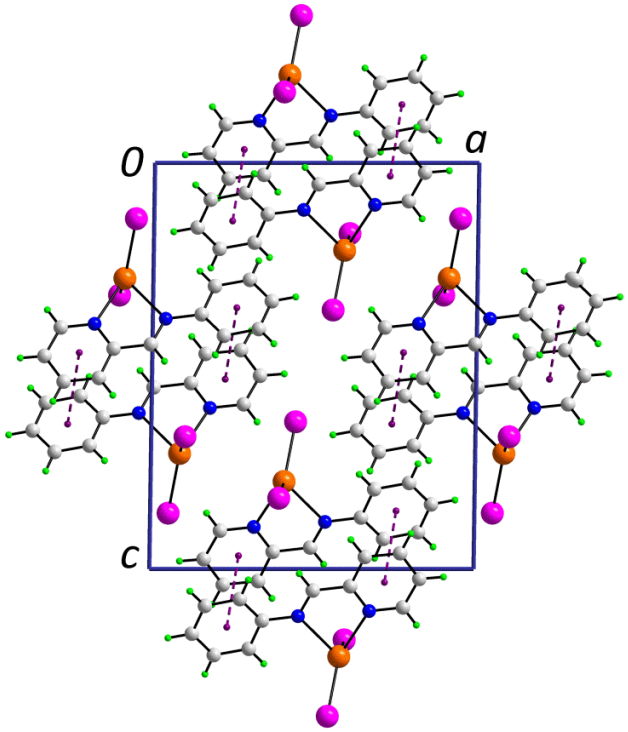

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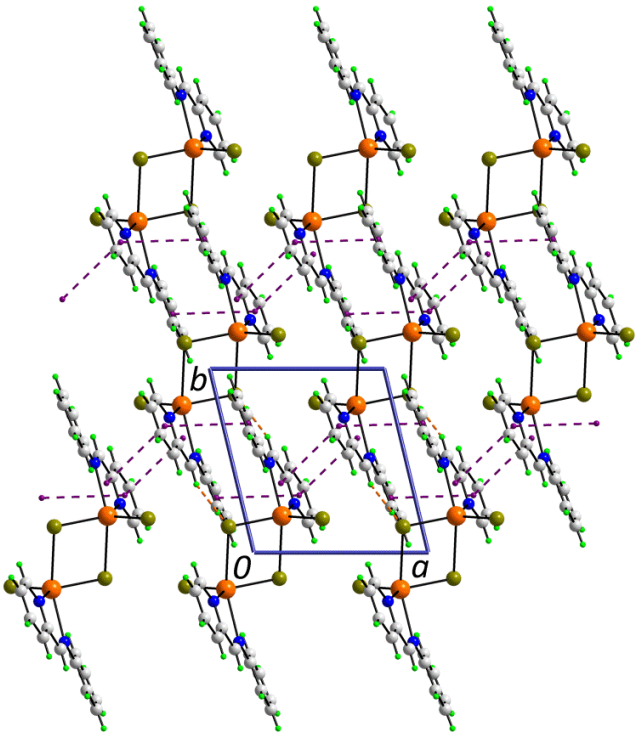

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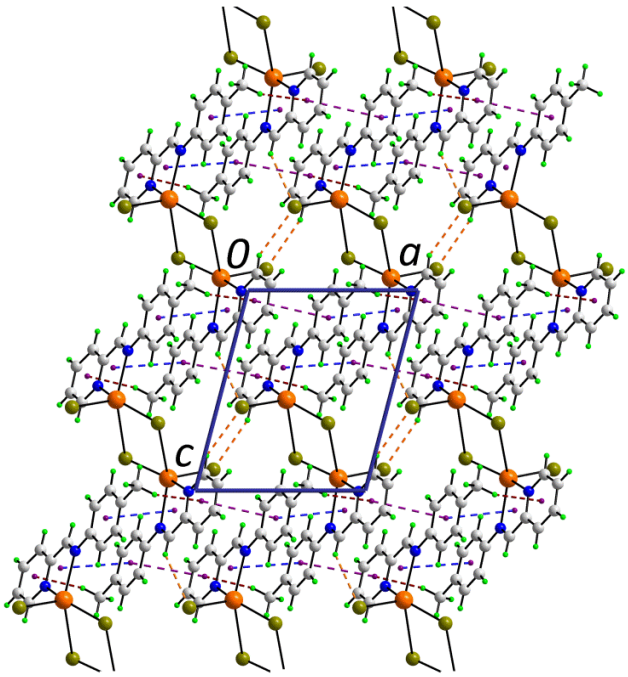

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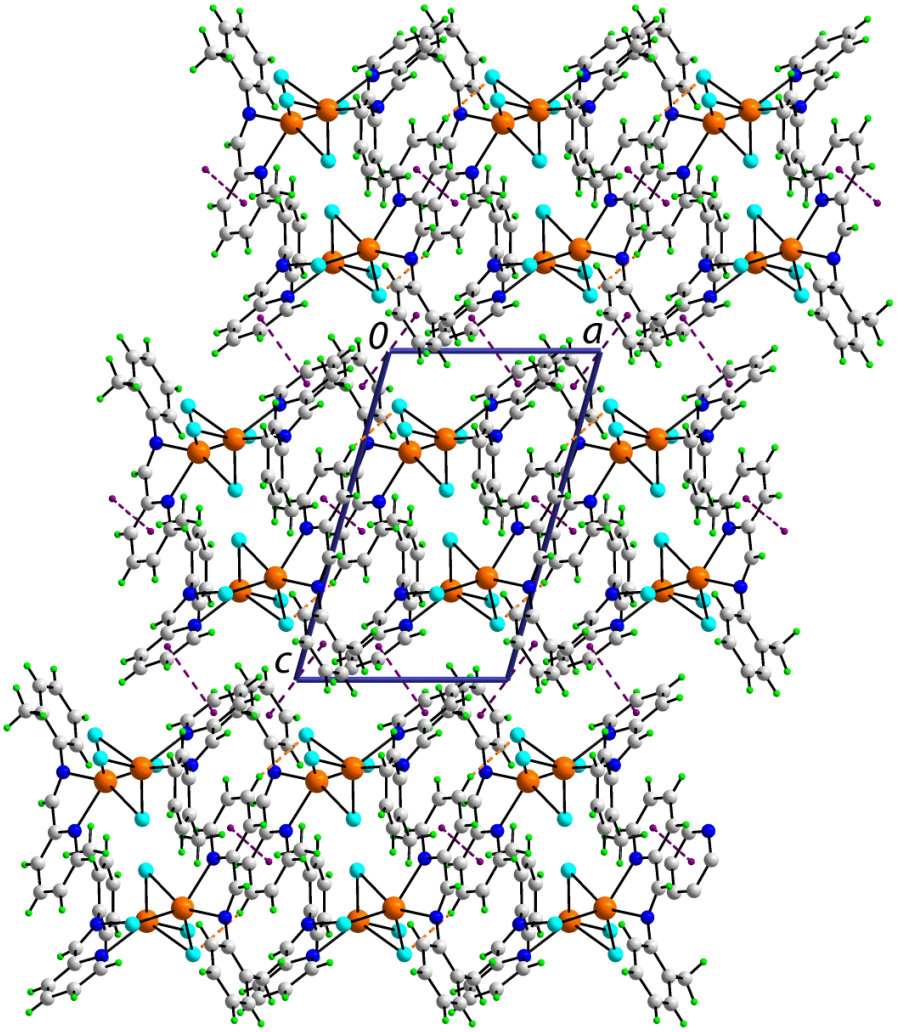

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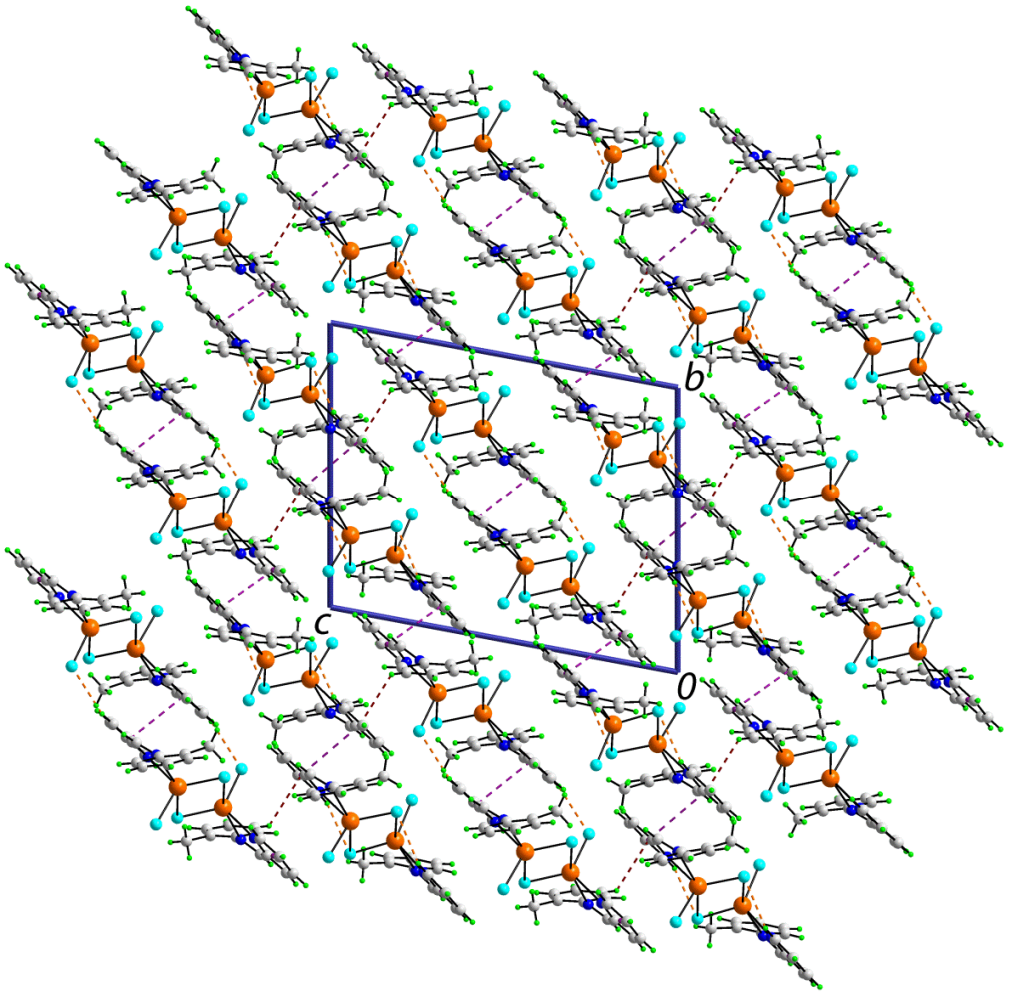

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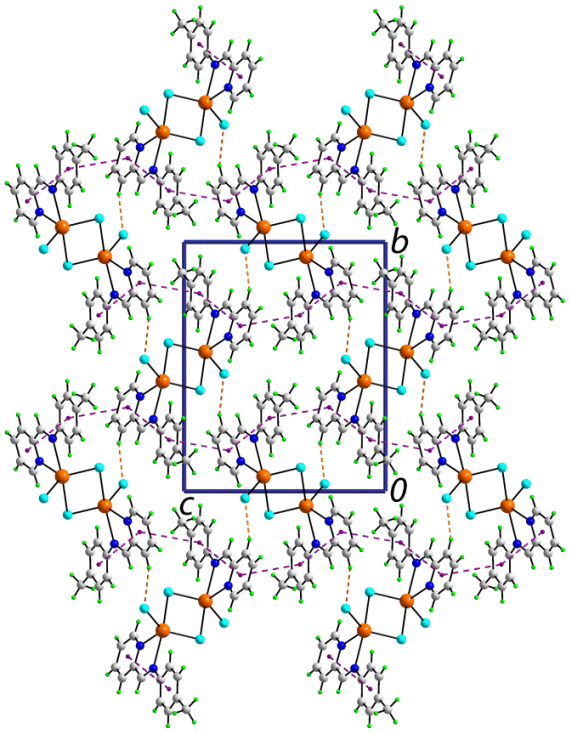

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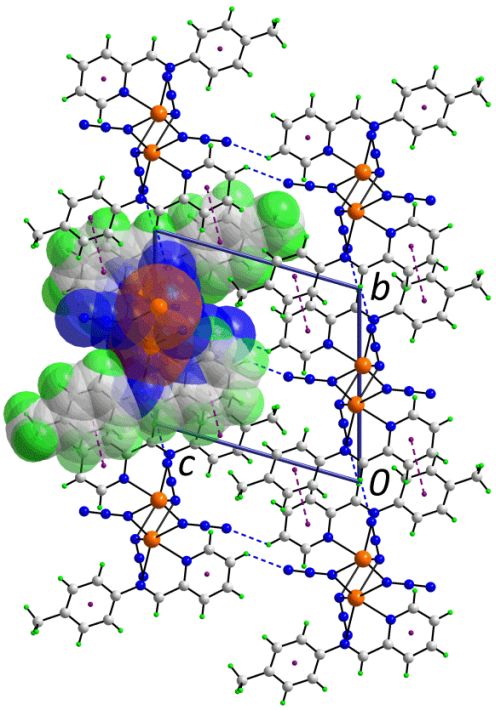

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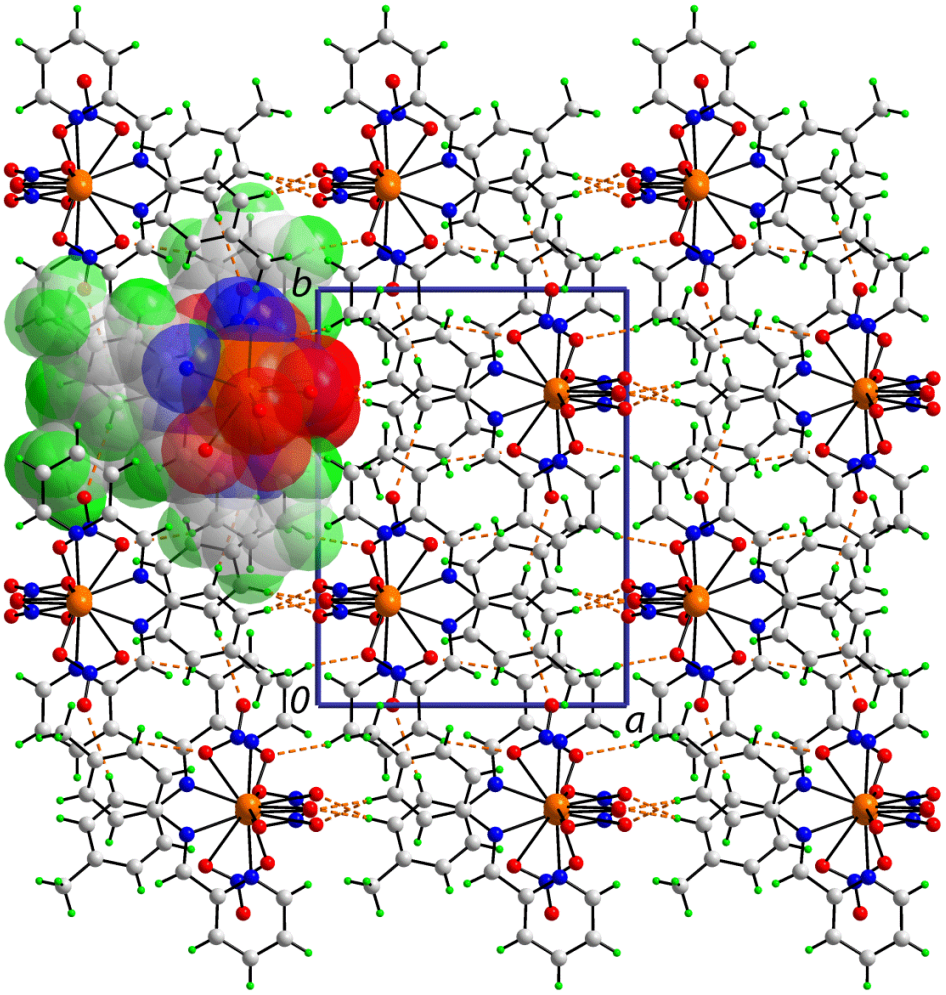

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