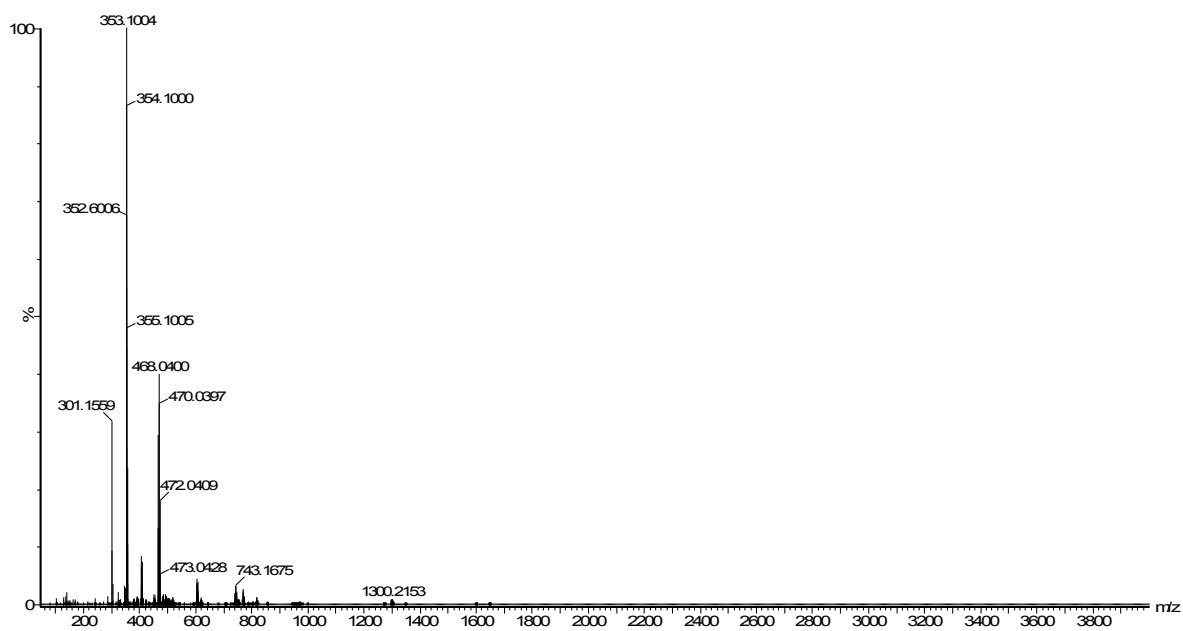


Flexibility and anion exchange of [(X)@Pd₂L₄] cages for recognition of size and charge of polyatomic anions

Jeyeong Lee,^a Sangwoo Lim,^a Dongwon Kim,^a Young-A Lee^{*b} and Ok-Sang Jung^{*a}

Electronic supplementary information (ESI) available: ESI-TOF-MS of [PdL₂](NO₃)₂; ¹H NMR spectra and IR spectra of 1,2-bis(dimethyl(pyridin-3-yl)silyl)ethane (L), [PdL₂](NO₃)₂, [(BF₄)@Pd₂L₄](BF₄)₃, [(ClO₄)@Pd₂L₄](ClO₄)₃·C₄H₈O₂, [(PF₆)@Pd₂L₄](PF₆)₃, [(ReO₄)@Pd₂L₄](ReO₄)₃·CH₄O and [(SiF₆)@Pd₂L₄](SiF₆)·8C₂H₆SO; DOSY spectra of [PdL₂](NO₃)₂ and [(BF₄)@Pd₂L₄](BF₄)₃; crystallographic data of [(BF₄)@Pd₂L₄](BF₄)₃, [(ClO₄)@Pd₂L₄](ClO₄)₃·C₄H₈O₂, [(PF₆)@Pd₂L₄](PF₆)₃, [(ReO₄)@Pd₂L₄](ReO₄)₃·CH₄O and [(SiF₆)@Pd₂L₄](SiF₆)·8C₂H₆SO. CCDC 2025726–2025730. For ESI and crystallographic data in CIF or other electronic format see DOI:



(a)

(b)

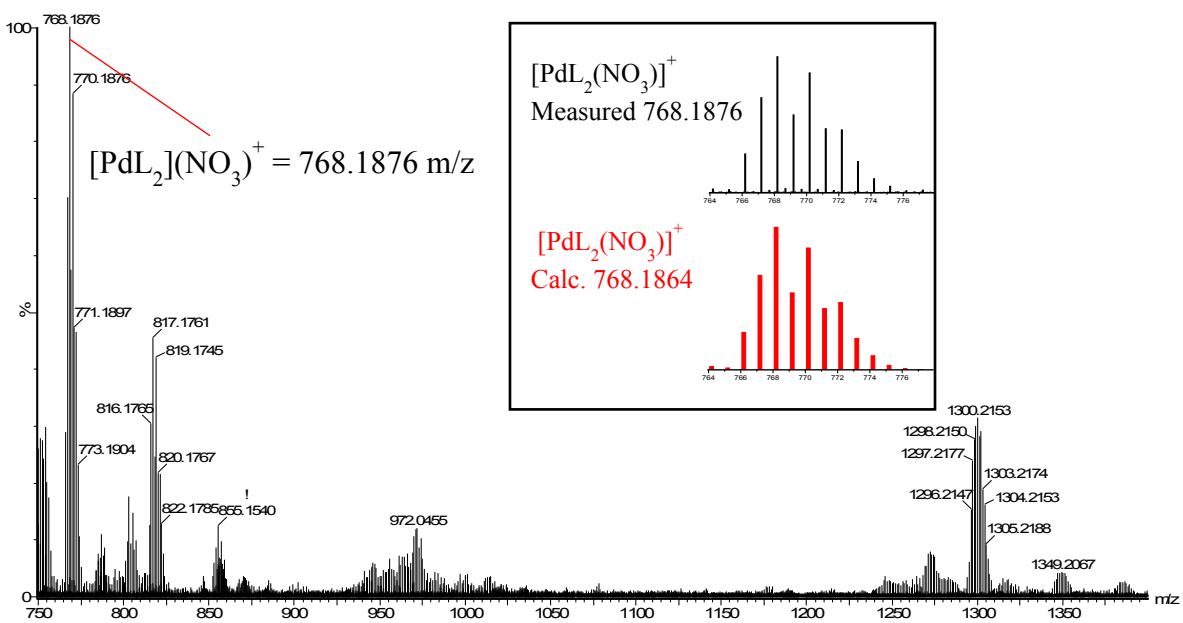


Fig. S1 Electrospray time of flight ionization mass spectrometry (ESI-TOF-MS) data of $[\text{PdL}_2](\text{NO}_3)_2$. m/z range 50-4000 (a), m/z range 750-1400 (b). m/z for $[\text{PdL}_2(\text{NO}_3)]^+ = 768.1876$

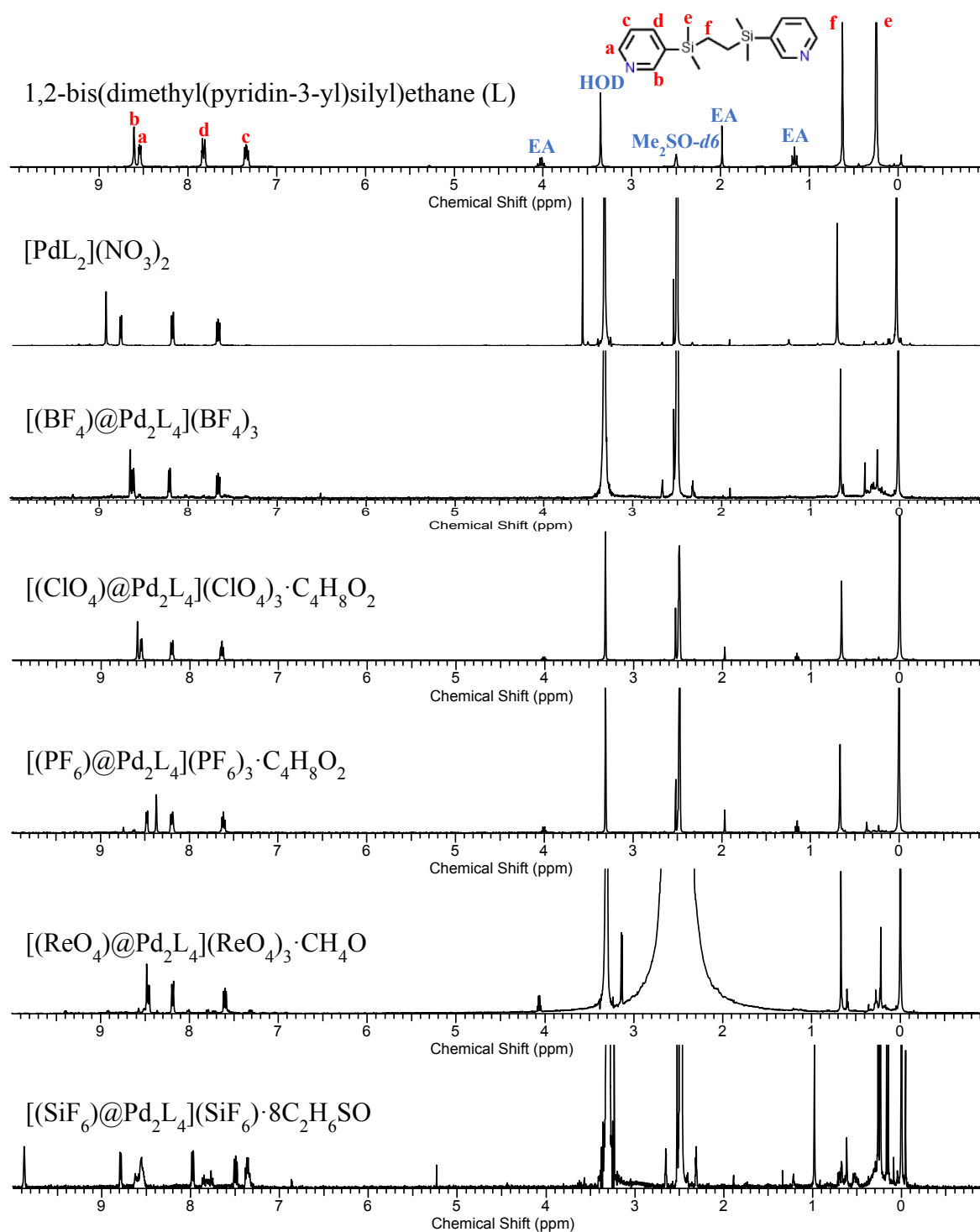
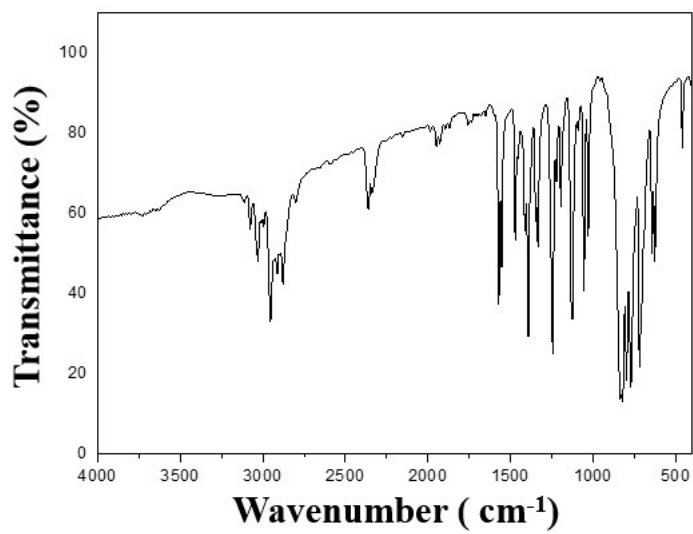
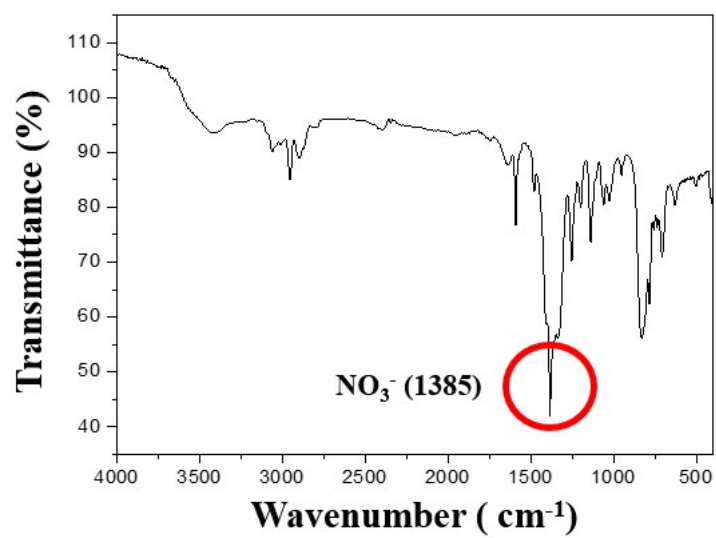


Fig. S2 ^1H NMR spectra of 1,2-bis(dimethyl(pyridin-3-yl)silyl)ethane (L), $[\text{PdL}_2](\text{NO}_3)_2$, $[(\text{BF}_4)@ \text{Pd}_2\text{L}_4](\text{BF}_4)_3$, $[(\text{ClO}_4)@ \text{Pd}_2\text{L}_4](\text{ClO}_4)_3 \cdot \text{C}_4\text{H}_8\text{O}_2$, $[(\text{PF}_6)@ \text{Pd}_2\text{L}_4](\text{PF}_6)_3 \cdot \text{C}_4\text{H}_8\text{O}_2$, $[(\text{ReO}_4)@ \text{Pd}_2\text{L}_4](\text{ReO}_4)_3 \cdot \text{CH}_4\text{O}$, $[(\text{SiF}_6)@ \text{Pd}_2\text{L}_4](\text{SiF}_6)_3 \cdot 8\text{C}_2\text{H}_6\text{SO}$.

1,2-bis(dimethyl(pyridin-3-yl)silyl)ethane (L)

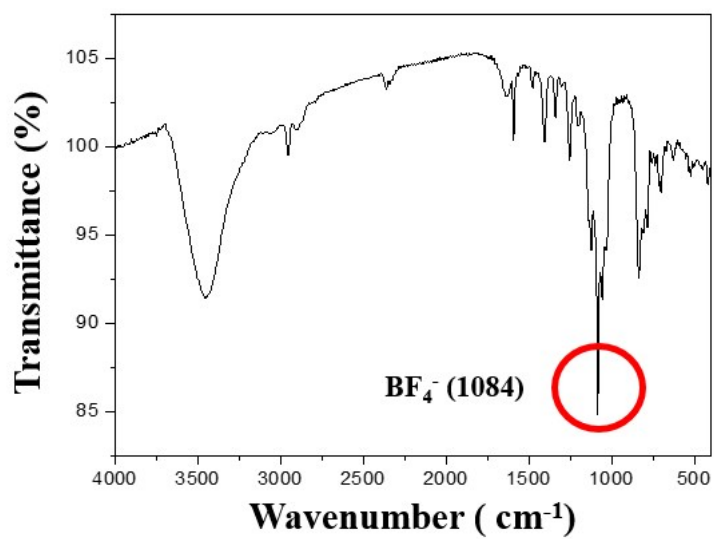


[PdL₂](NO₃)₂

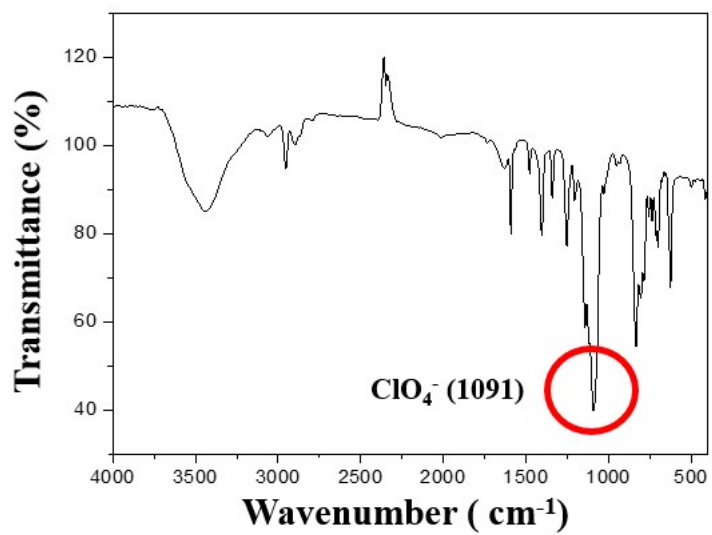


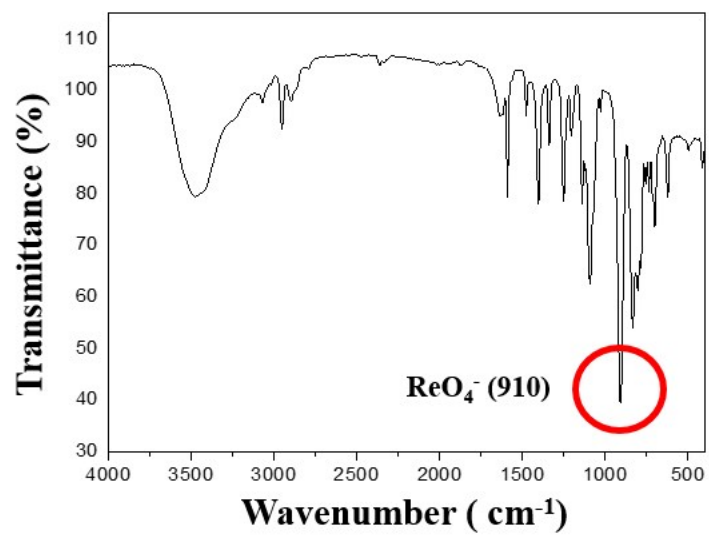
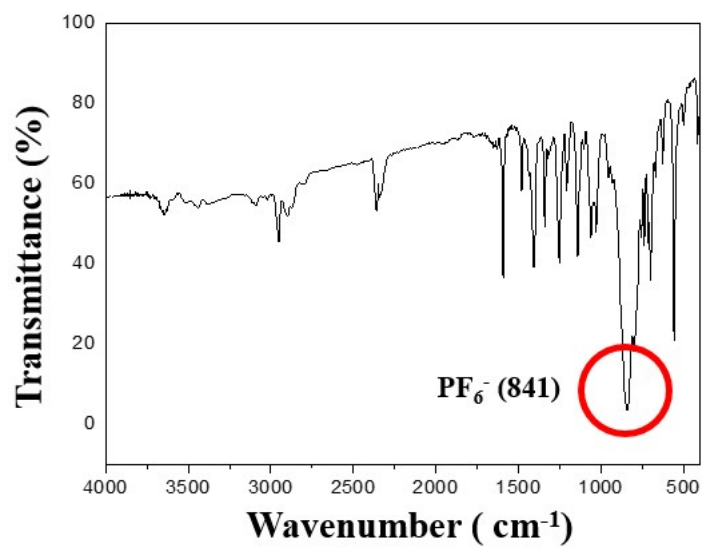
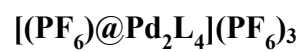
[(BF₄)

@Pd₂L₄](BF₄)₃



[(ClO₄)@Pd₂L₄](ClO₄)₃·C₄H₈O₂





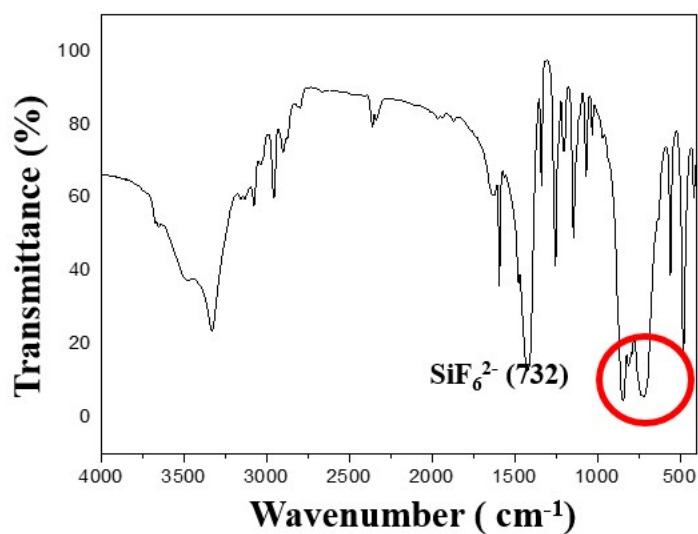
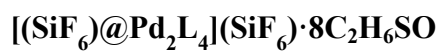
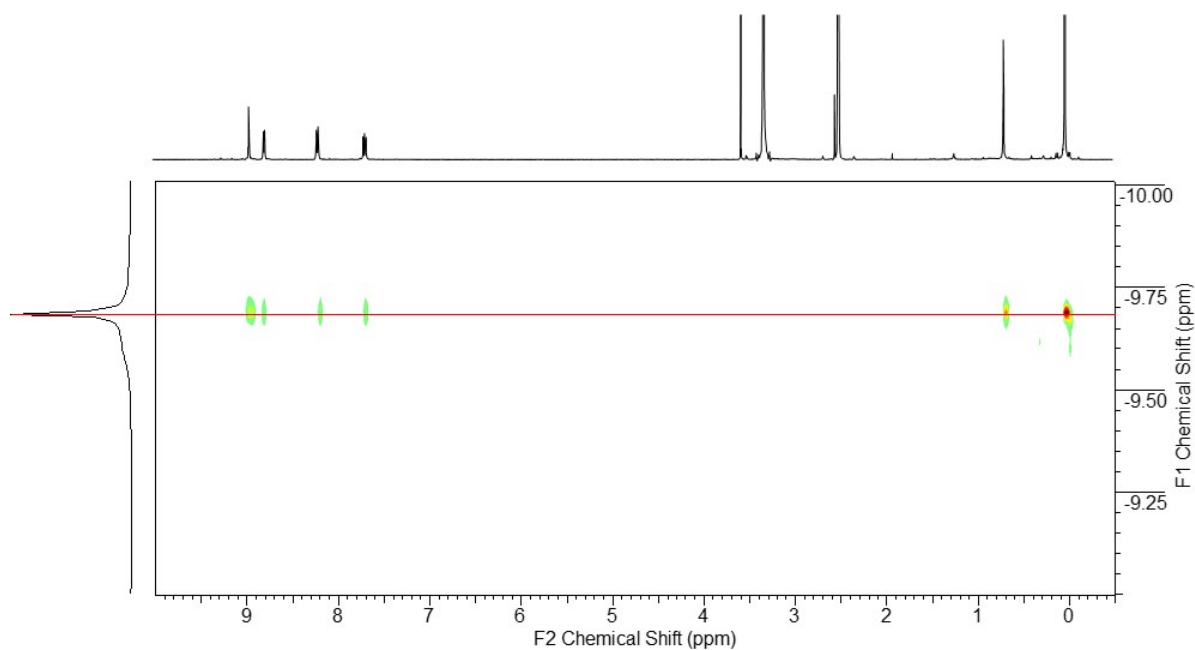


Fig. S3 IR spectra of 1,2-bis(dimethyl(pyridin-3-yl)silyl)ethane (L), $[\text{PdL}_2](\text{NO}_3)_2$, $[(\text{BF}_4)@\text{Pd}_2\text{L}_4](\text{BF}_4)_3$, $[(\text{ClO}_4)@\text{Pd}_2\text{L}_4](\text{ClO}_4)_3 \cdot \text{C}_4\text{H}_8\text{O}_2$, $[(\text{PF}_6)@\text{Pd}_2\text{L}_4](\text{PF}_6)_3$, $[(\text{ReO}_4)@\text{Pd}_2\text{L}_4](\text{ReO}_4)_3 \cdot \text{CH}_4\text{O}$, $[(\text{SiF}_6)@\text{Pd}_2\text{L}_4](\text{SiF}_6) \cdot 8\text{C}_2\text{H}_6\text{SO}$.

(a)



(b)

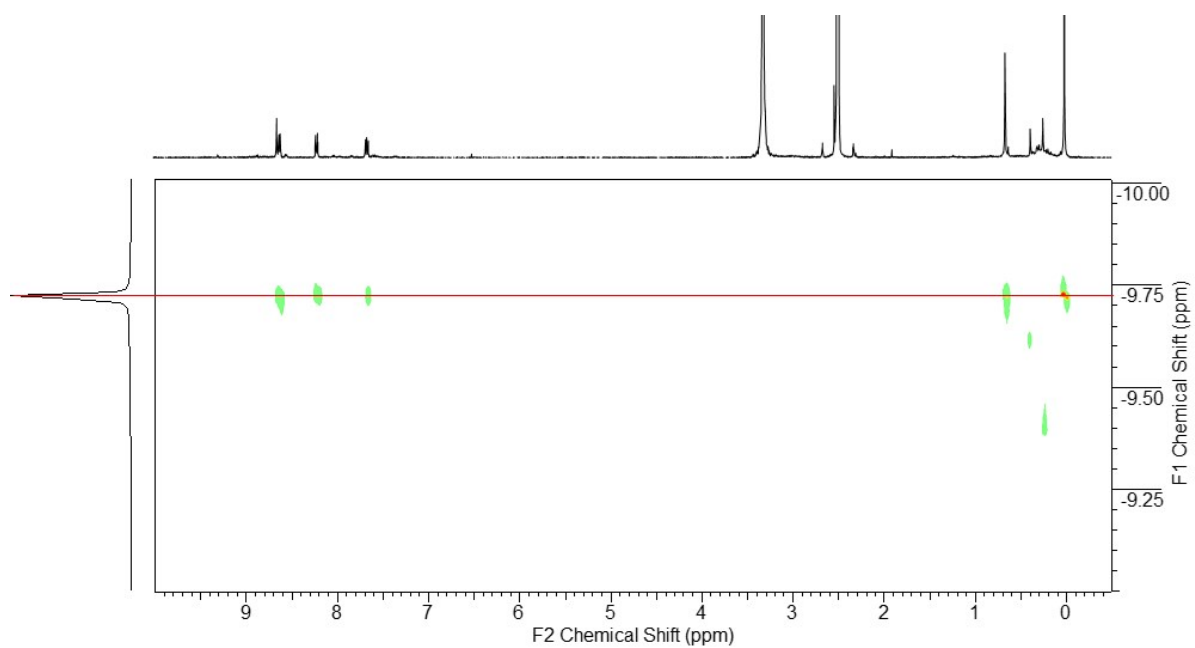
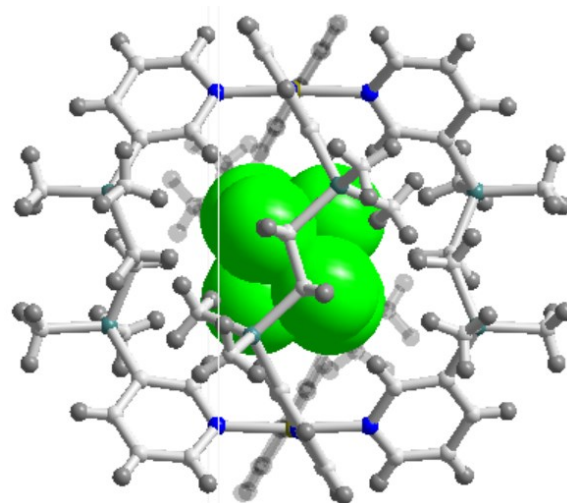
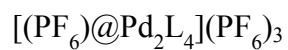
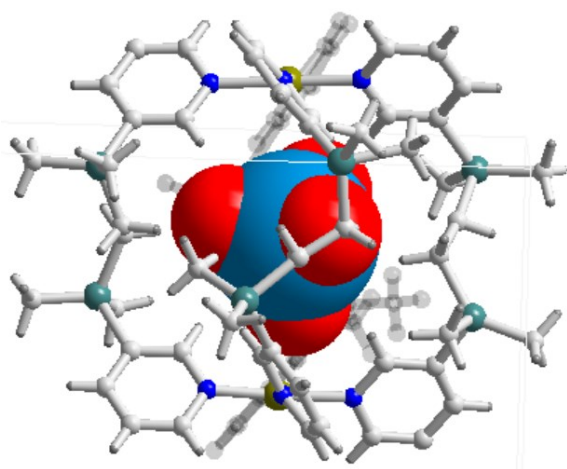
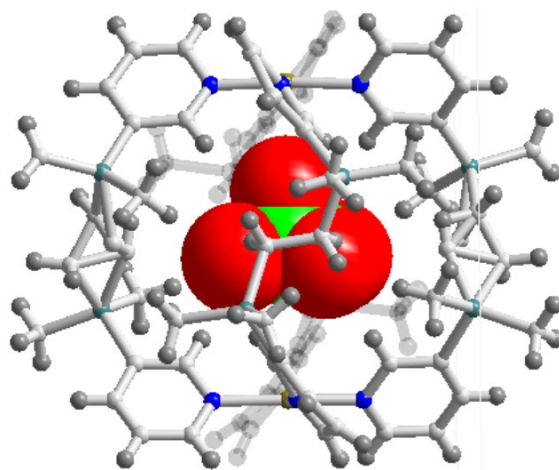
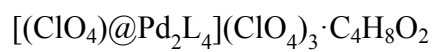
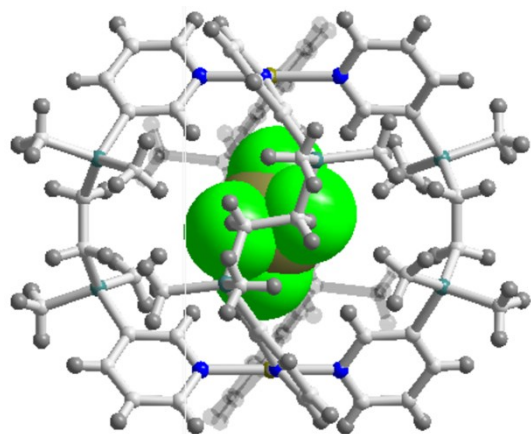
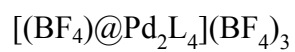
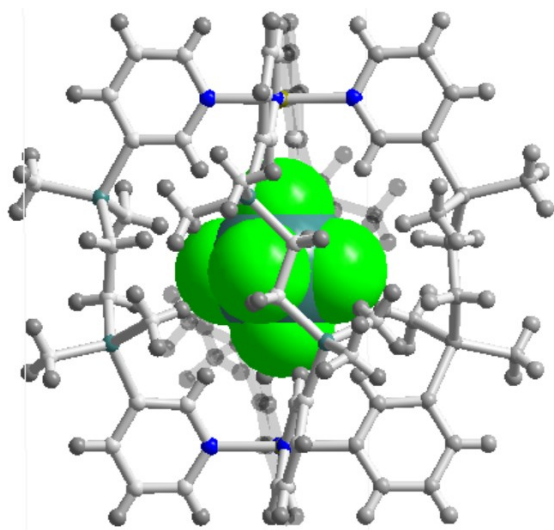
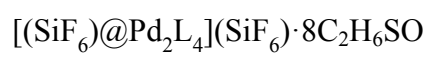


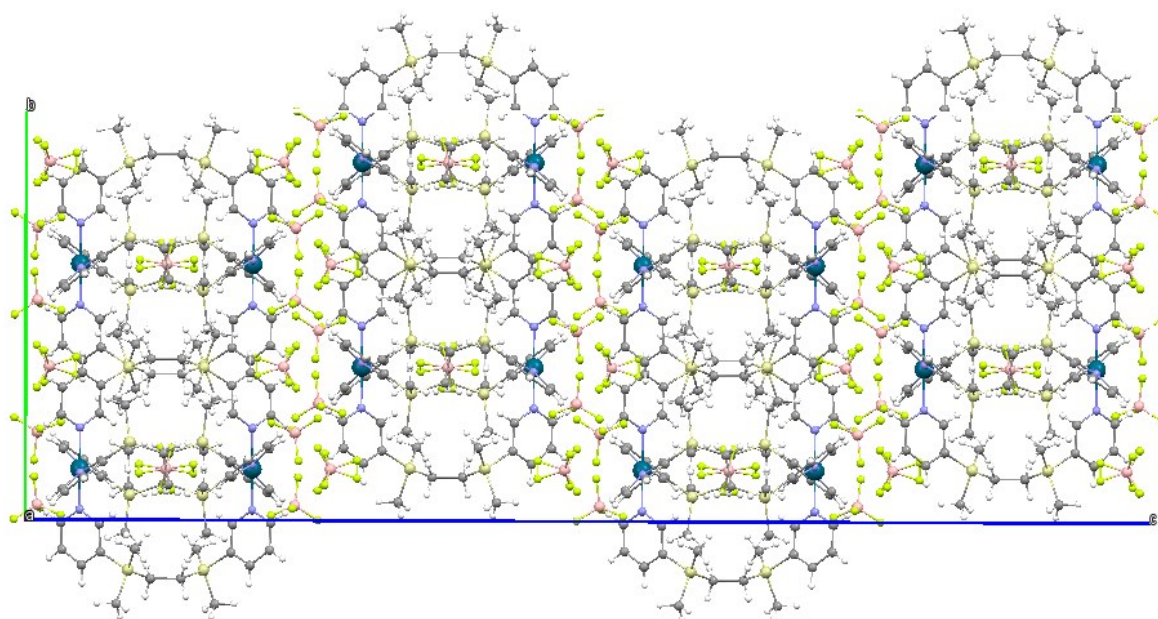
Fig. S4 DOSY spectra of $[\text{PdL}_2](\text{NO}_3)_2$ (a) and $[(\text{BF}_4)@ \text{Pd}_2\text{L}_4](\text{BF}_4)_3$ (b) in $\text{Me}_2\text{SO}-d^6$ at 298 K. For the (a), $D = 2.11 \times 10^{-11}$, $\log D = -9.685$. For the (b), $D = 1.97 \times 10^{-11}$, $\log D = -9.726$.

Fig. S5 X-ray structure of $[(\text{BF}_4)@ \text{Pd}_2\text{L}_4](\text{BF}_4)_3$, $[(\text{ClO}_4)@ \text{Pd}_2\text{L}_4](\text{ClO}_4)_3 \cdot \text{C}_4\text{H}_8\text{O}_2$, $[(\text{ReO}_4)@ \text{Pd}_2\text{L}_4](\text{ReO}_4)_3 \cdot \text{CH}_4\text{O}$, $[(\text{PF}_6)@ \text{Pd}_2\text{L}_4](\text{PF}_6)_3$, $[(\text{SiF}_6)@ \text{Pd}_2\text{L}_4](\text{SiF}_6)_3 \cdot 8\text{C}_2\text{H}_6\text{SO}$.

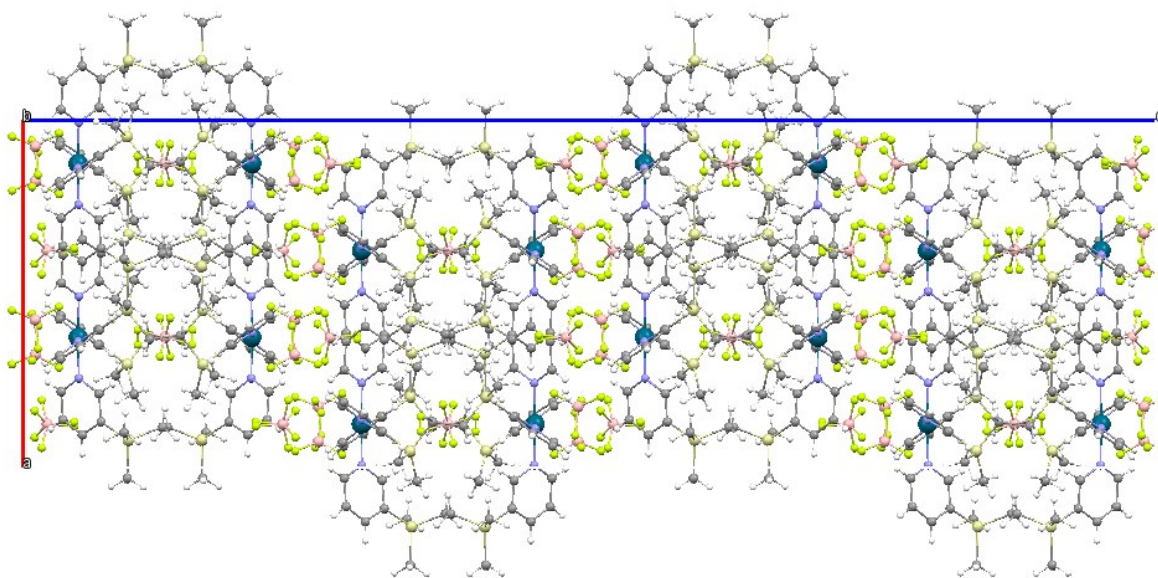




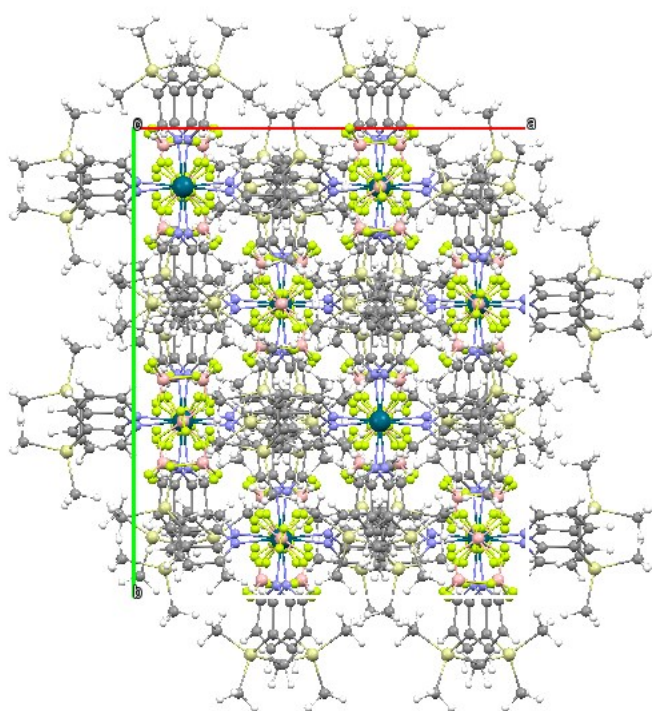
(a) $[(\text{BF}_4)@\text{Pd}_2\text{L}_4](\text{BF}_4)_3$



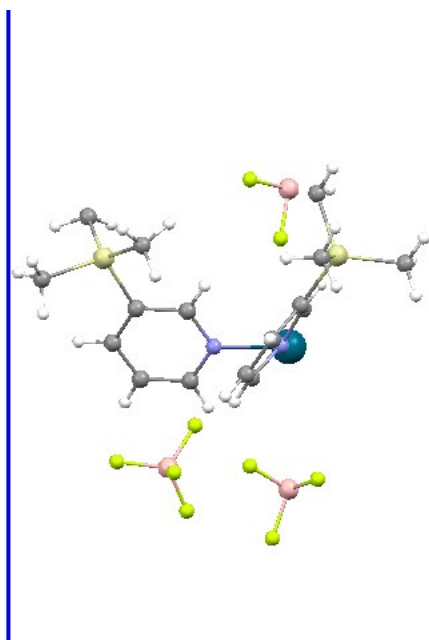
Packing structure (*a*-axis)



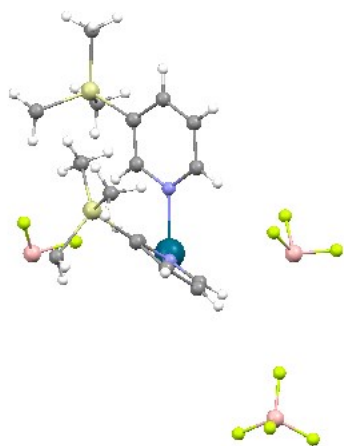
Packing structure (*b*-axis)



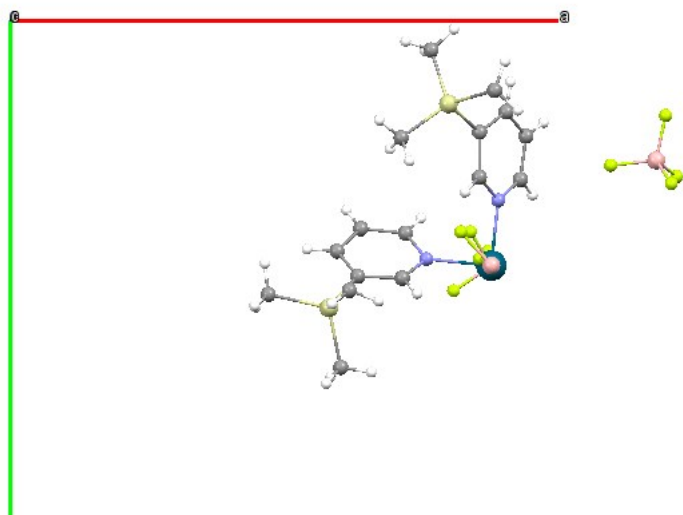
Packing structure (c-axis)



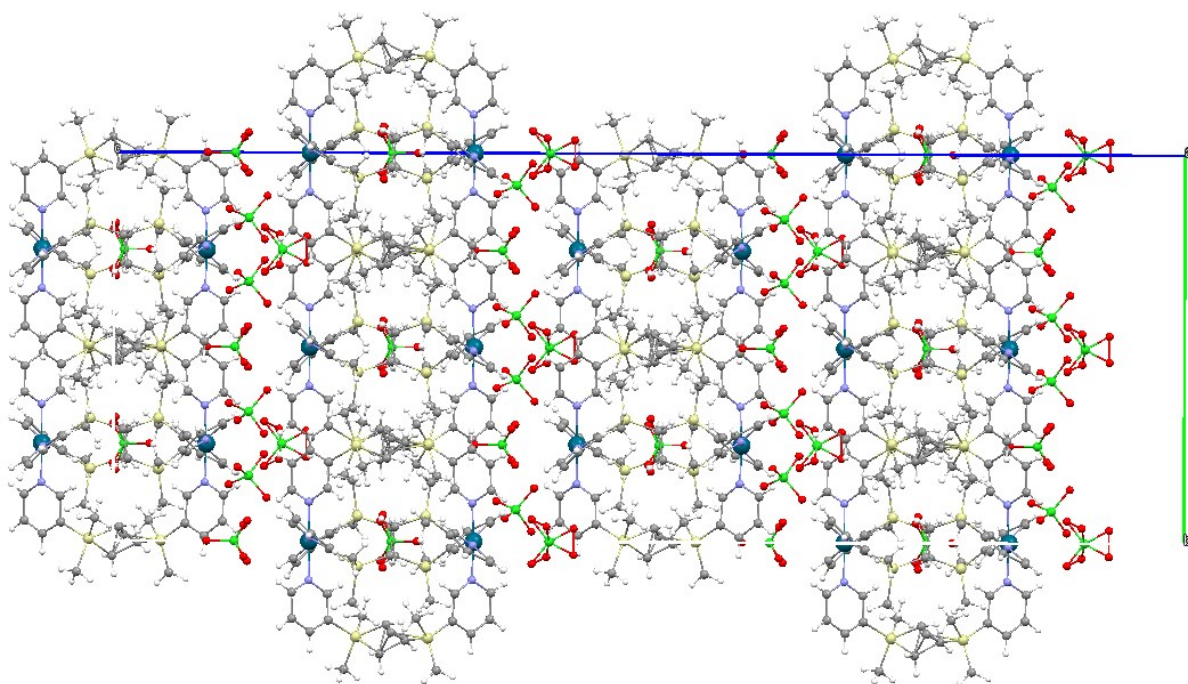
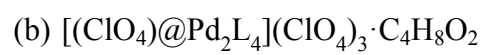
Asymmetric unit (a-axis)



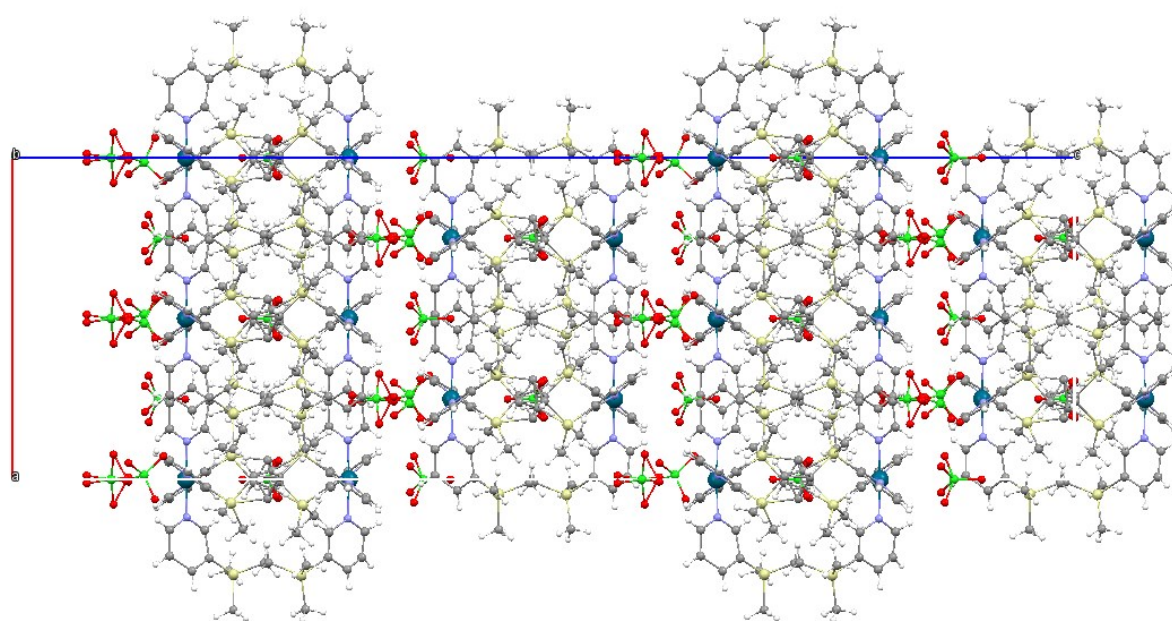
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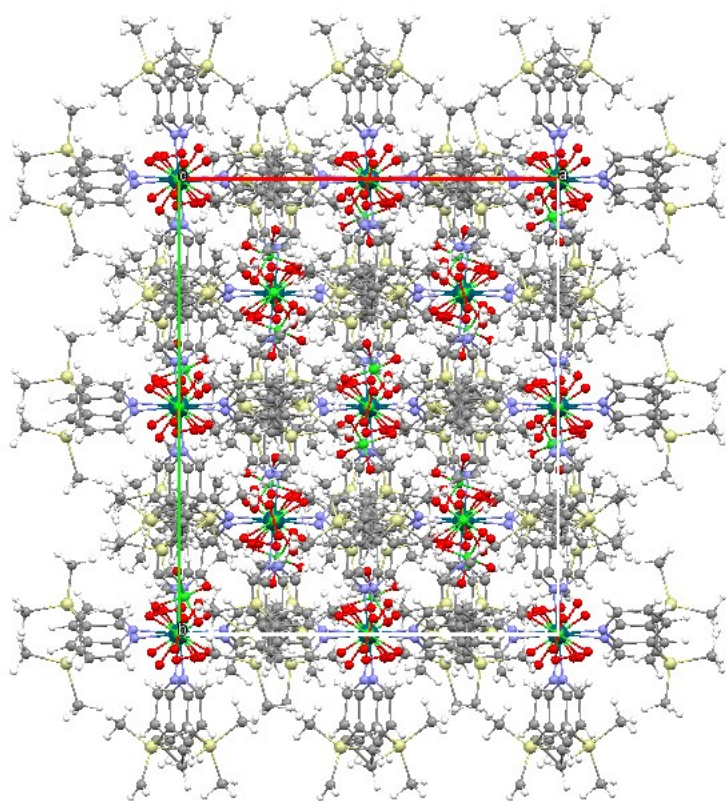
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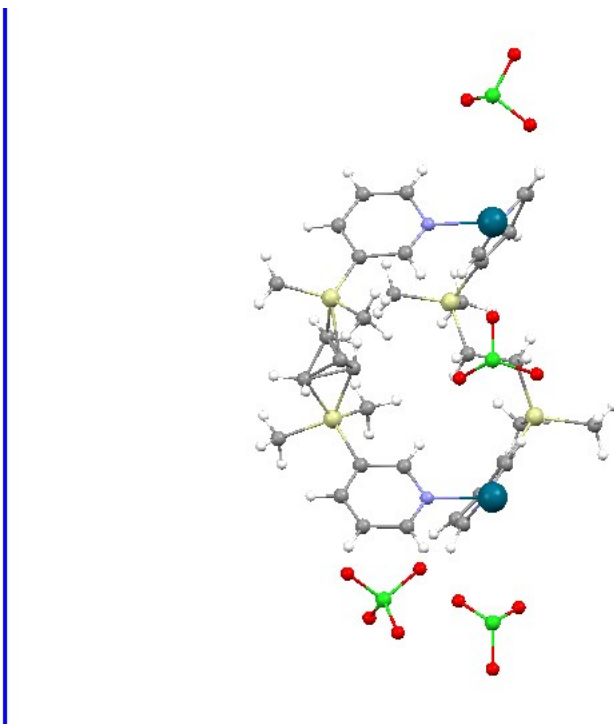
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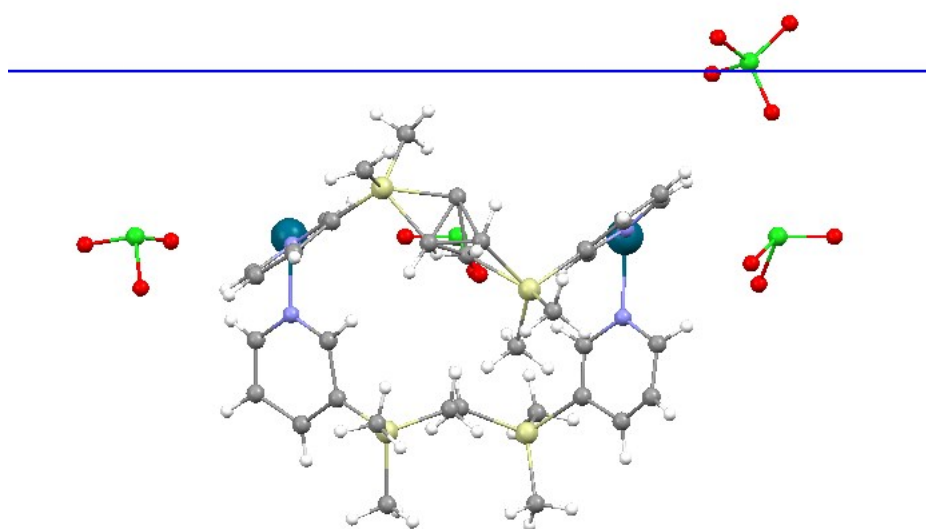
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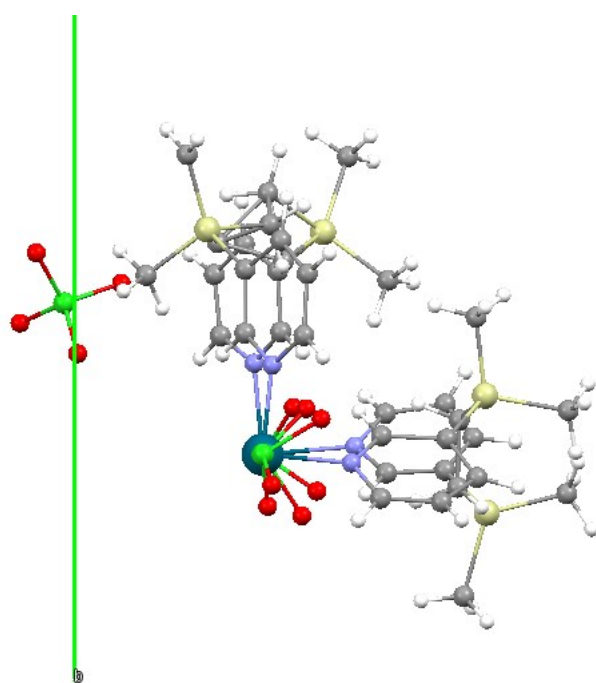
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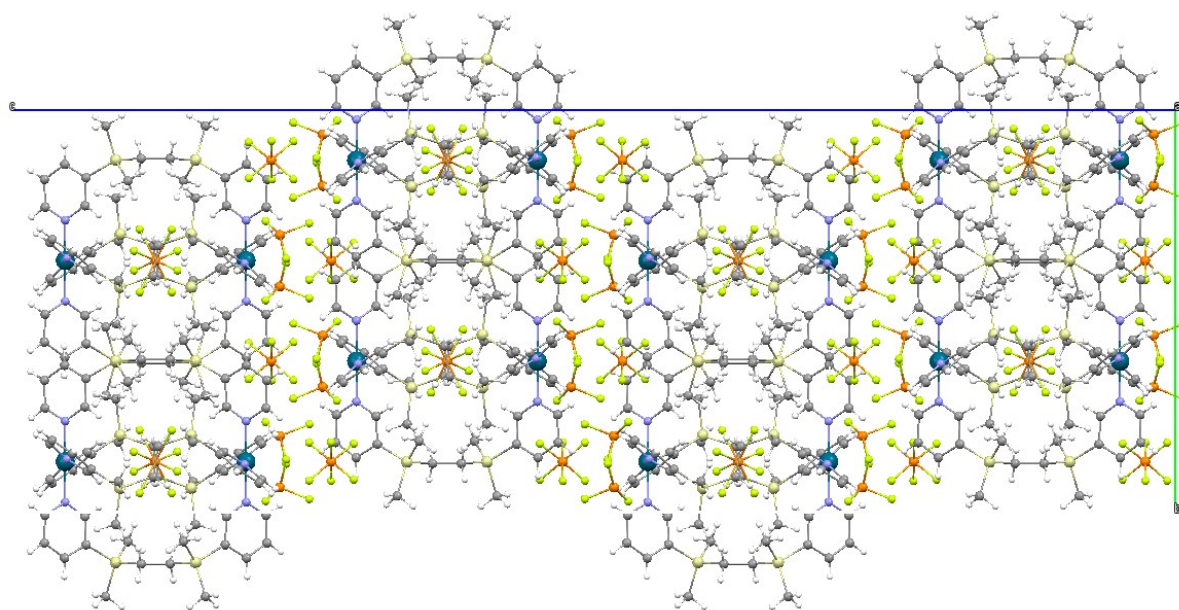
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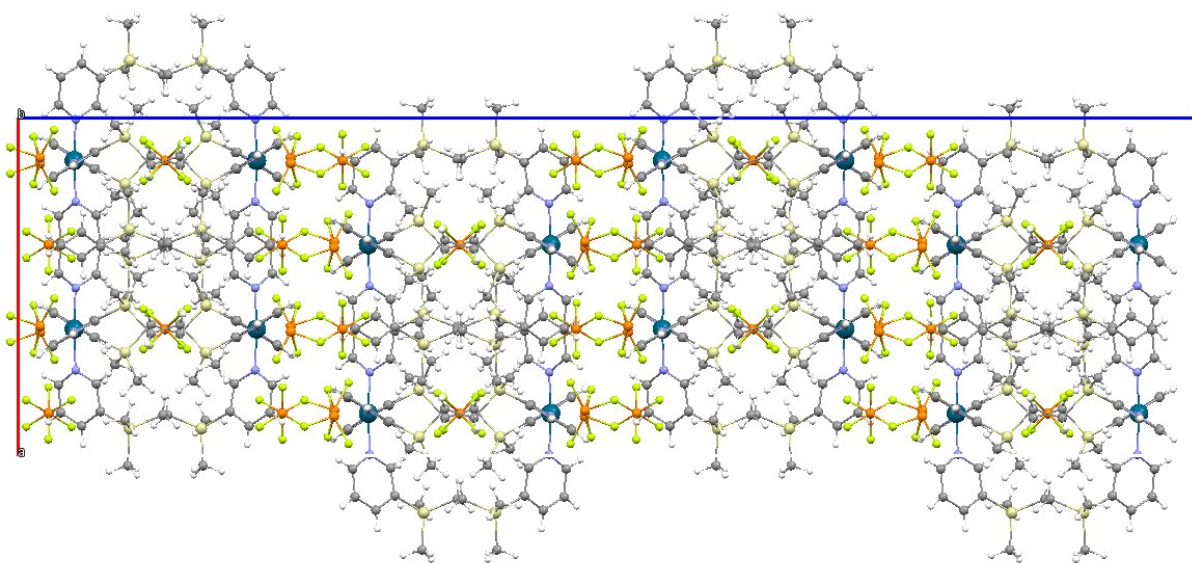
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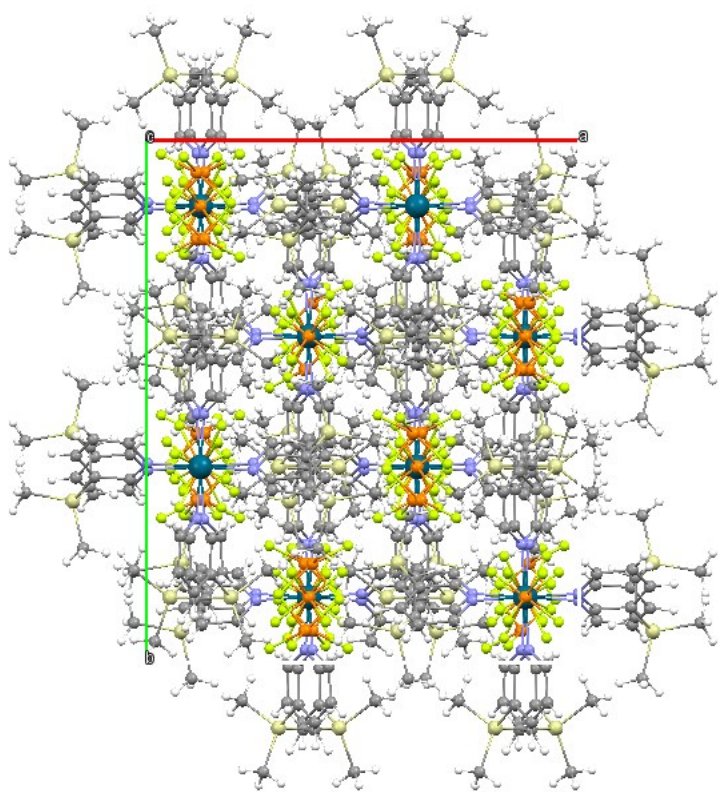
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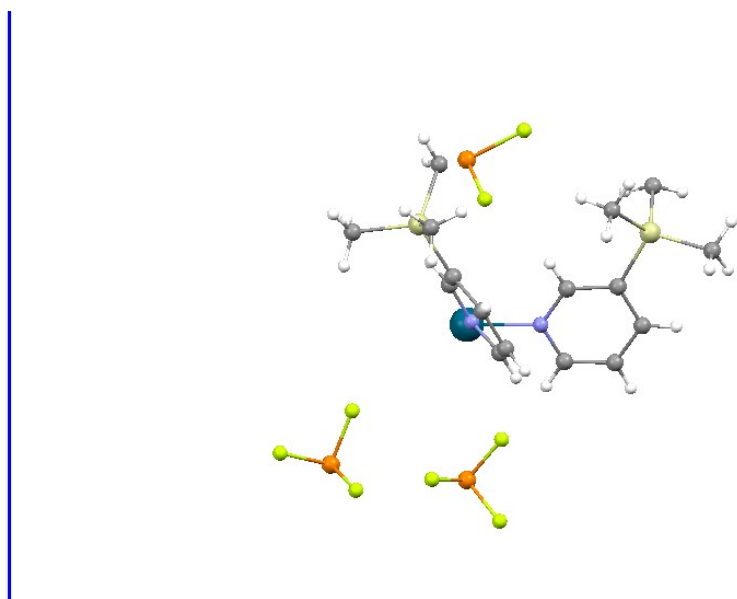
Packing structure (a-axis)



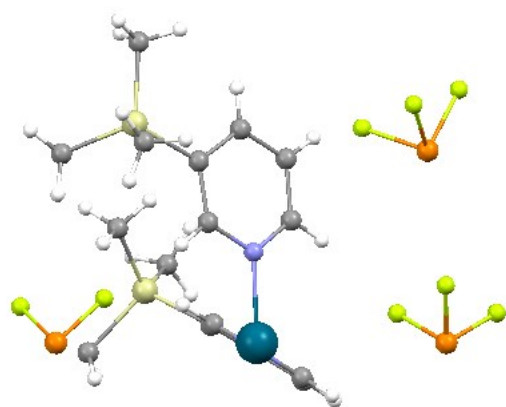
Packing structure (b-axis)



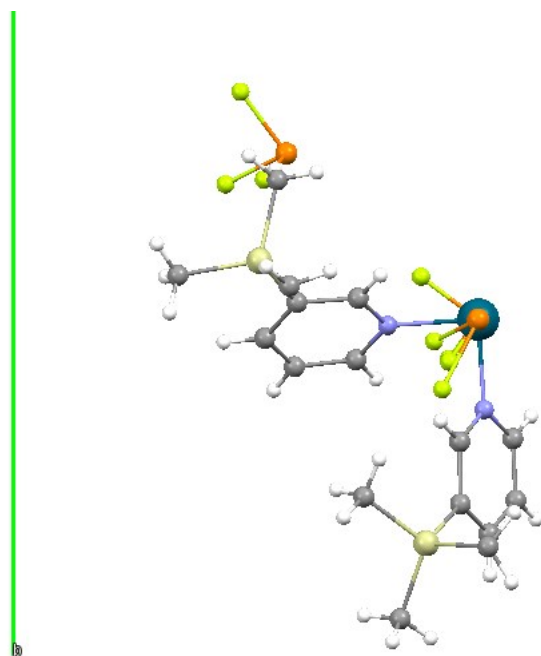
Packing structure (c-axis)



Asymmetric unit (a-axis)

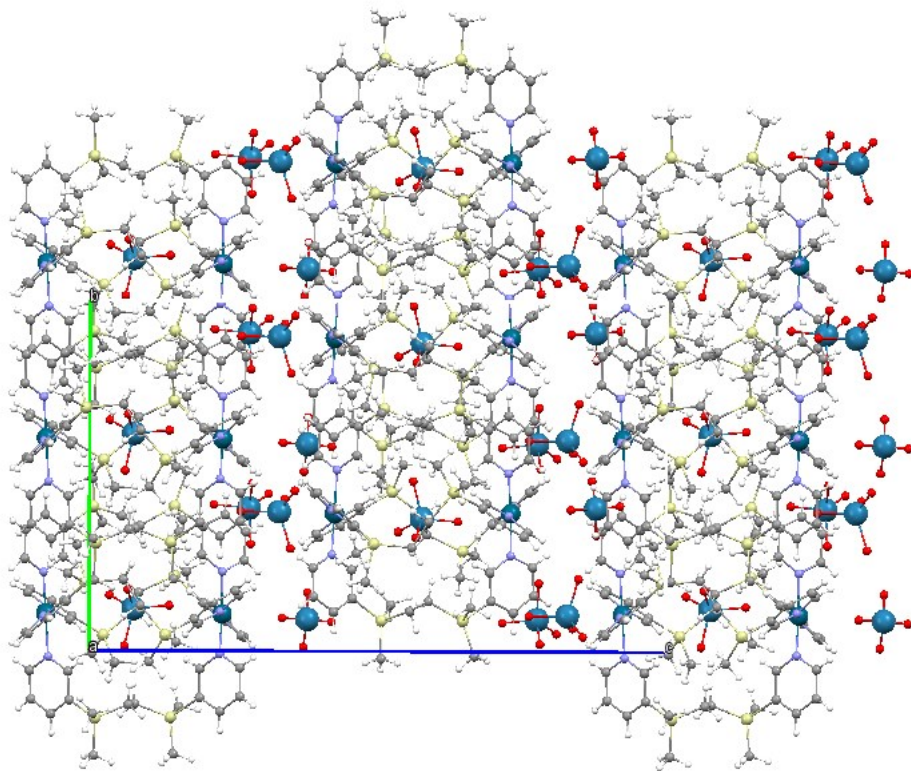


Asymmetric unit (b-axis)

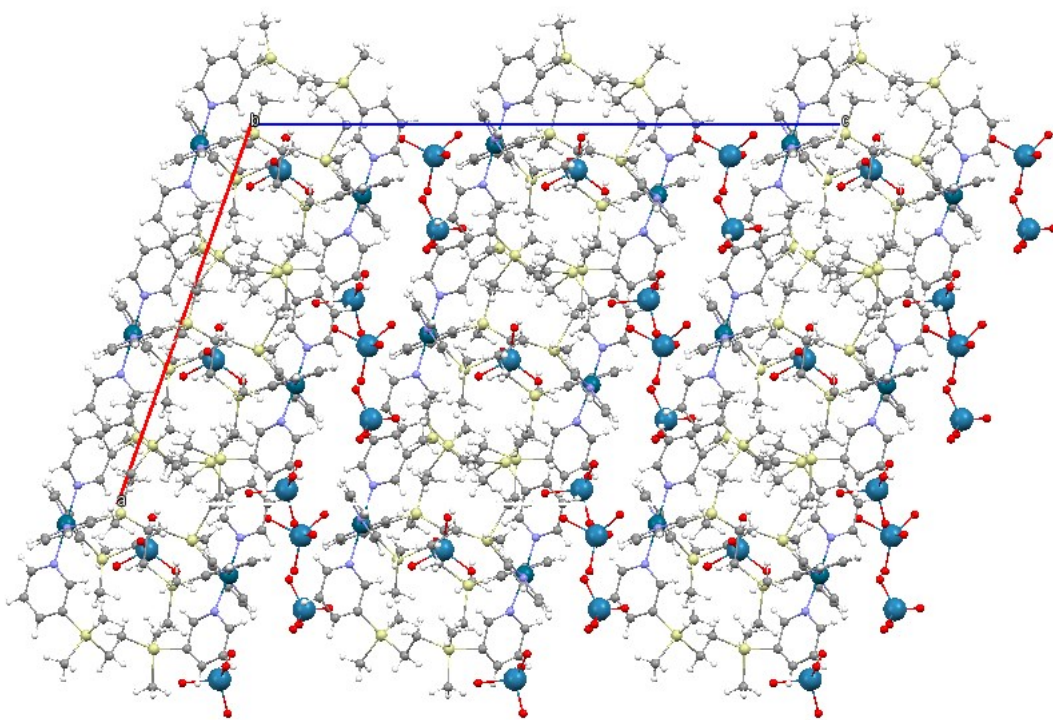


Asymmetric unit (c-axis)

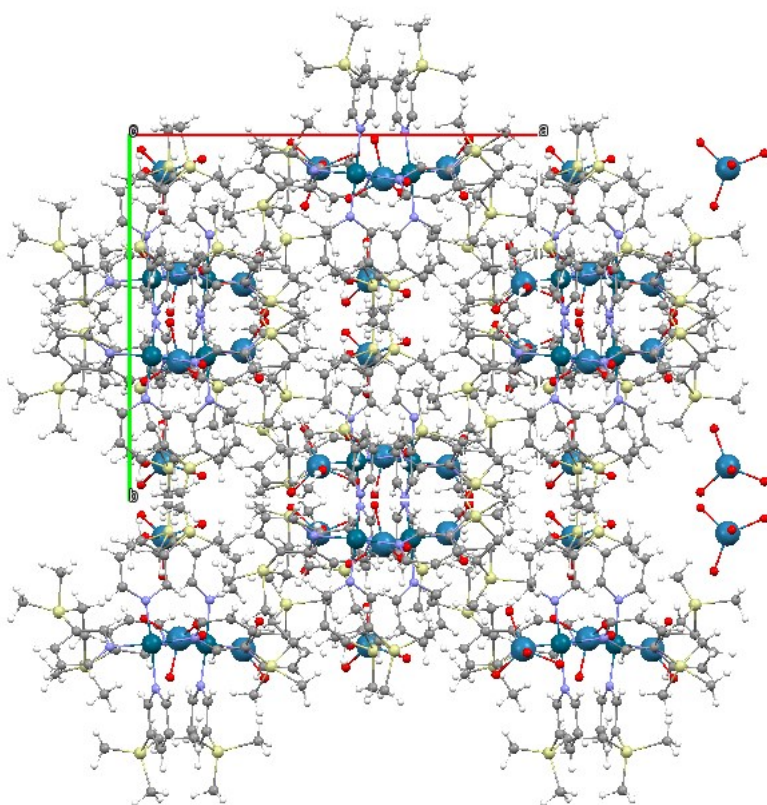
(d) $[(\text{ReO}_4)@(\text{Pd}_2\text{L}_4)](\text{ReO}_4)_3 \cdot \text{CH}_4\text{O}$



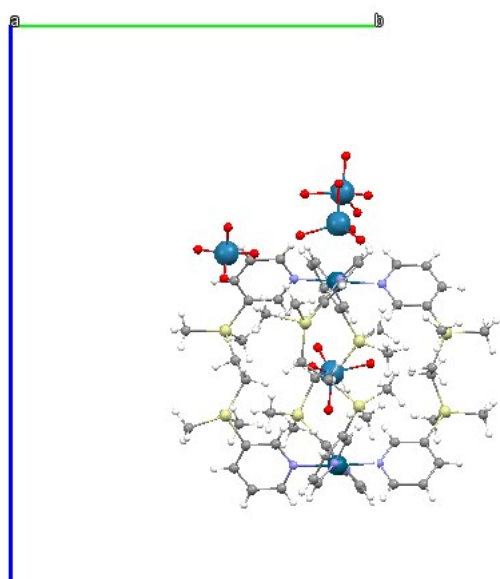
Packing structure (a-axis)



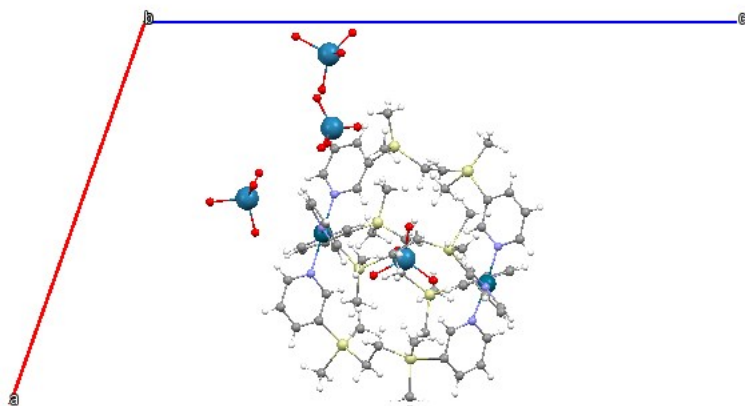
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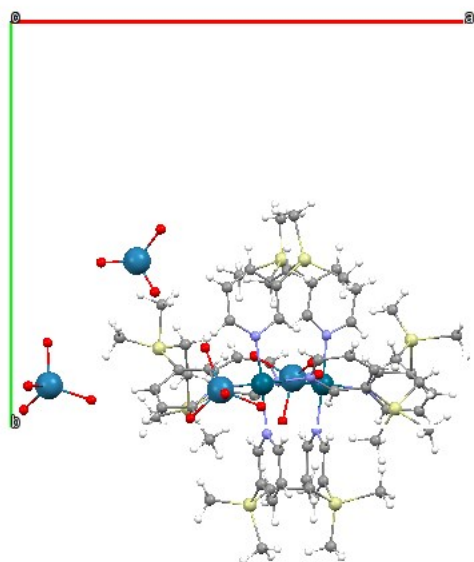
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Asymmetric unit (a-axis)

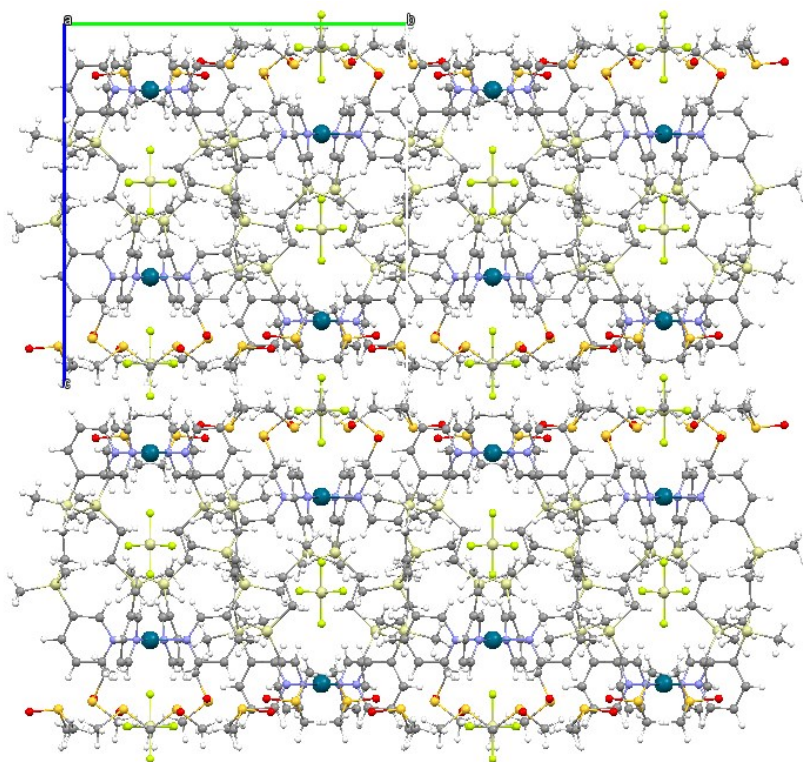


Asymmetric unit (b-axis)

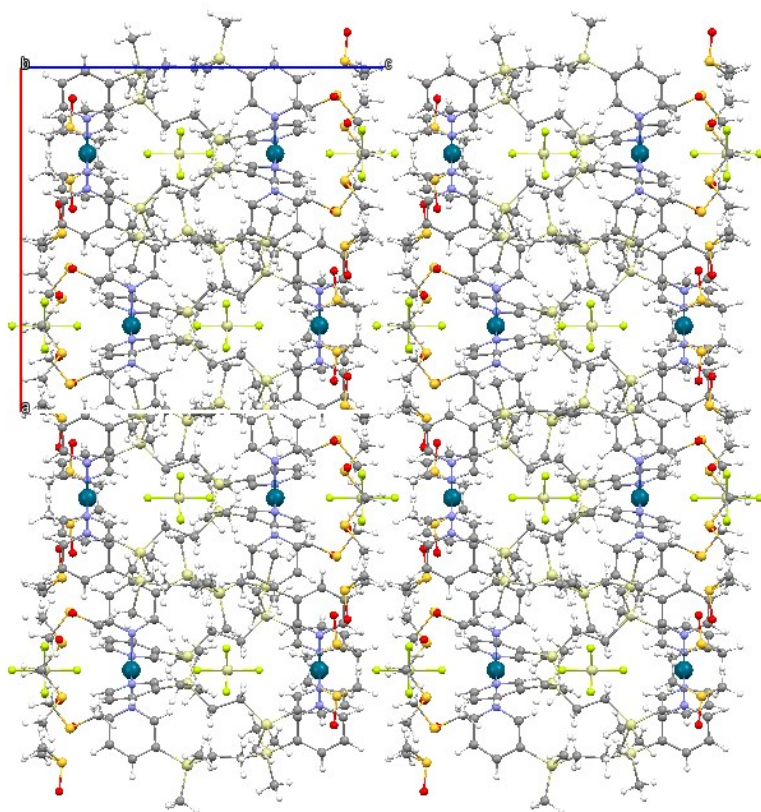


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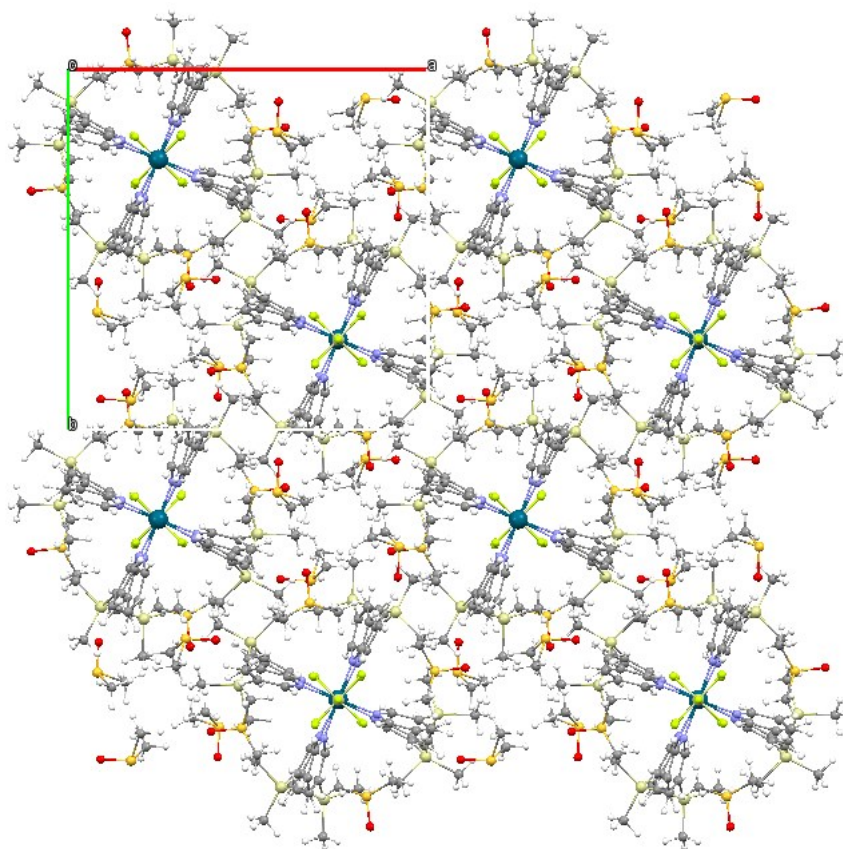
(e) $[(\text{SiF}_6)@\text{Pd}_2\text{L}_4](\text{SiF}_6) \cdot 8\text{C}_2\text{H}_6\text{SO}$



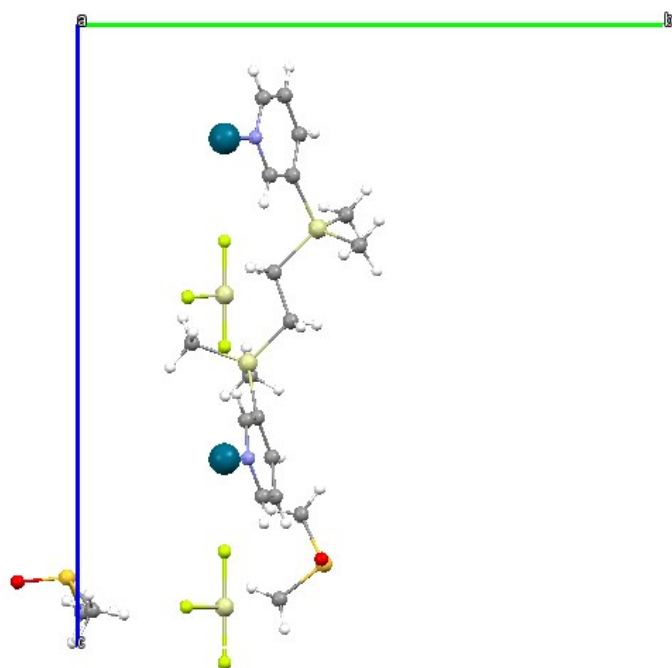
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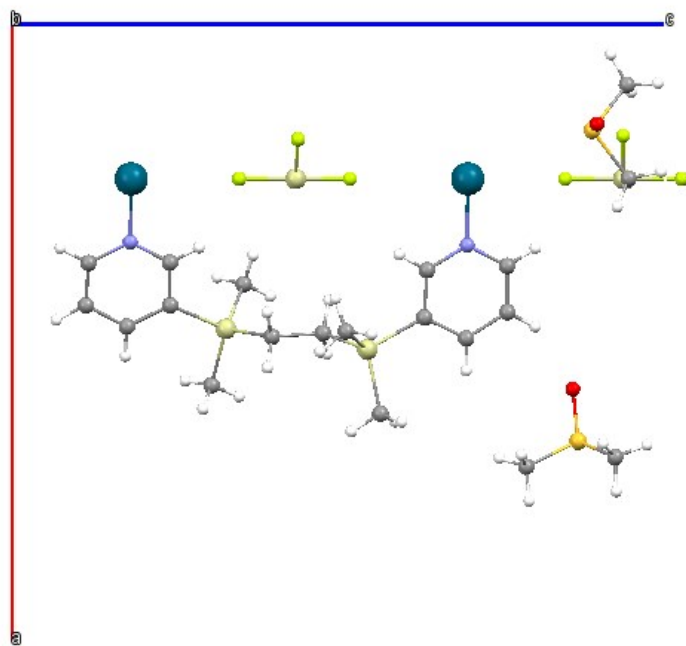
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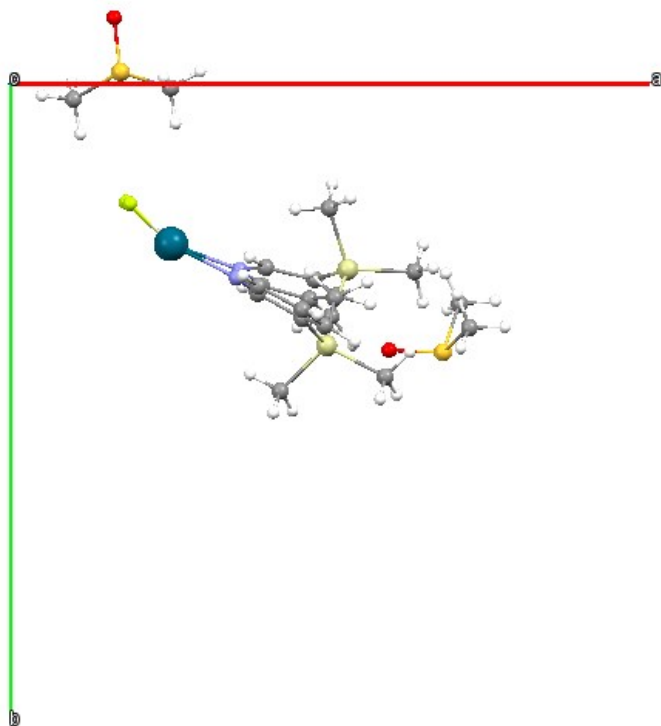
Packing structure (c-axis)



Asymmetric unit (a-axis)



Asymmetric unit (b-axis)



Asymmetric unit (c-axis)