Supplementary Material (ESI) for Dalton Transactions

Pentachloro(pyrazine)rhenate(IV) Complex as Precursor of heterobimetallic pyrazine-containing $Re^{IV}_2M^{II}$ (M = Ni, Cu) Species : Synthesis, Crystal Structures and Magnetic Properties

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Supporting information

Table S1 Selected interatomic distances (Å) and angles (°) for compounds **1-3** with esds in parentheses[a] (*Rhenium environment*).

cat = NBu_4^+ (**1**)

Re(1)-N(1)	2.173(2)	Re(1)-Cl(3)	2.353(1)
Re(1)-Cl(1)	2.320(1)	Re(1)-Cl(4)	2.340(1)
Re(1)-Cl(2)	2.336(1)	Re(1)-Cl(5)	2.340(1)
N(1)-Re(1)-Cl(1)	178.53(5)	Cl(1)-Re(1)-Cl(5)	91.46(3)
N(1)-Re(1)-Cl(2)	89.53(5)	Cl(2)-Re(1)-Cl(3)	89.72(2)
N(1)-Re(1)-Cl(3)	87.30(5)	Cl(2)-Re(1)-Cl(4)	89.47(2)
N(1)-Re(1)-Cl(4)	88.10(5)	Cl(2)-Re(1)-Cl(5)	177.31(2)
N(1)-Re(1)-Cl(5)	87.94(5)	Cl(3)-Re(1)-Cl(4)	175.33(2)
Cl(1)-Re(1)-Cl(2)	91.08(3)	Cl(3)-Re(1)-Cl(5)	91.10(2)
Cl(1)-Re(1)-Cl(3)	91.36(2)	Cl(4)-Re(1)-Cl(5)	89.50(2)
Cl(1)-Re(1)-Cl(4)	93.25(3)		

cat = $NH_2Me_2^+$ (**2**)

Re(1)-N(1)	2.156(4)	Re(1)-Cl(2)	2.353(1)
Re(1)-Cl(1)	2.348(1)	Re(1)-Cl(3)	2.344(1)
N(1)-Re(1)-Cl(1)	179.5(1)	Cl(1)-Re(1)-Cl(3)	91.51(4)
N(1)-Re(1)-Cl(2)	88.43(7)	Cl(2)-Re(1)-Cl(3)	89.20(3)
N(1)-Re(1)-Cl(3)	88.87(8)	Cl(2c)-Re(1)-Cl(3)	177.27(3)
Cl(1)-Re(1)-Cl(2)	91.18(4)		

cat = NH_4^+ (**3**)

Re(1)-N(1)	2.150(5)	Re(2)-N(3)	2.150(6)
Re(1)-Cl(1)	2.345(2)	Re(2)-Cl(4)	2.336(2)
Re(1)-Cl(2)	2.365(1)	Re(2)-Cl(5)	2.335(1)
Re(1)-Cl(3)	2.321(1)	Re(2)-Cl(6)	2.350(1)
N(1)-Re(1)-Cl(1)	177.8(2)	N(3)-Re(2)-Cl(4)	179.8(2)
N(1)-Re(1)-Cl(2)	88.3(1)	N(3)-Re(2)-Cl(5)	88.9(1)
N(1)-Re(1)-Cl(3)	88.6(1)	N(3)-Re(2)-Cl(6)	88.4(1)
Cl(1)-Re(1)-Cl(2)	90.19(5)	Cl(4)-Re(2)-Cl(5)	91.21(5)
Cl(1)-Re(1)-Cl(3)	92.89(5)	Cl(4)-Re(2)-Cl(6)	91.43(5)
Cl(2)-Re(1)-Cl(3)	176.89(4)	Cl(5)-Re(2)-Cl(6)	177.34(5)
Cl(2)-Re(1)-Cl(3b)	89.41(5)	Cl(5)-Re(2)-Cl(6c)	89.80(5)
Cl(2)-Re(1)-Cl(2b)	90.11(6)	Cl(5)-Re(2)-Cl(5c)	89.76(7)
Cl(3)-Re(1)-Cl(3b)	90.90(7)	Cl(6)-Re(2)-Cl(6c)	90.52(7)
Cl(3b)-Re(1)-Cl(2b)	176.89(4)	Cl(5c)-Re(2)-Cl(6c)	177.34(5)

[a] Symmetry transformations used to generate equivalent atoms: (b) *x*, -*y*+1, *z*; (c) *x*, -*y*, *z*

Table S2 Selected interatomic distances (Å) and angles (°) for compound **4** with esds in parentheses[a]

Rhenium environment

Re(1)-N(1)	2.174(3)	Re(1)-Cl(3)	2.324(1)
Re(1)-Cl(1)	2.312(1)	Re(1)-Cl(4)	2.363(1)
Re(1)-Cl(2)	2.357(1)	Re(1)-Cl(5)	2.335(1)
N(1)-Re(1)-Cl(1)	177.03(9)	Cl(1)-Re(1)-Cl(5)	93.43(5)
N(1)-Re(1)-Cl(2)	86.5(1)	Cl(2)-Re(1)-Cl(3)	91.60(4)
N(1)-Re(1)-Cl(3)	88.28(9)	Cl(2)-Re(1)-Cl(4)	88.89(4)
N(1)-Re(1)-Cl(4)	88.69(9)	Cl(2)-Re(1)-Cl(5)	175.61(4)
N(1)-Re(1)-Cl(5)	89.5(1)	Cl(3)-Re(1)-Cl(4)	176.90(4)
Cl(1)-Re(1)-Cl(2)	90.50(5)	Cl(3)-Re(1)-Cl(5)	90.21(5)
Cl(1)-Re(1)-Cl(3)	92.13(5)	Cl(4)-Re(1)-Cl(5)	89.08(4)
Cl(1)-Re(1)-Cl(4)	90.93(4)	Re(1)-Cl(2)···Ni(1)	124.5(1)

Nickel environment

Ni(1)-N(3)	1.945(3)	Ni(1)-N(4)	1.944(3)
Ni(1)···Cl(2)	3.221(1)		
N(3)-Ni(1)-N(4)	92.8(2)	N(3)-Ni(1)-N(3a)	180.0(1)
N(3)-Ni(1)-N(4a)	87.3(2)	N(4)-Ni(1)-N(4a)	180.0(1)

[a] Symmetry transformations used to generate equivalent atoms: (a) 1-*x*, 2 -*y*, -*z*.

Table S3 Selected interatomic distances (Å) and angles (°) for compound **5** with esds in parentheses[a]

Rhenium enviroment

Re(1)-N(1)	2.186(2)	Re(1)-Cl(3)	2.354(1)
Re(1)-Cl(1)	2.305(1)	Re(1)-Cl(4)	2.344(1)
Re(1)-Cl(2)	2.352(1)	Re(1)-Cl(5)	2.332(1)
N(1)-Re(1)-Cl(1)	179.33(5)	Cl(1)-Re(1)-Cl(5)	92.26(3)
N(1)-Re(1)-Cl(2)	87.55(5)	Cl(2)-Re(1)-Cl(3)	90.06(2)
N(1)-Re(1)-Cl(3)	87.79(5)	Cl(2)-Re(1)-Cl(4)	175.12(2)
N(1)-Re(1)-Cl(4)	87.63(5)	Cl(2)-Re(1)-Cl(5)	90.34(3)
N(1)-Re(1)-Cl(5)	88.19(5)	Cl(3)-Re(1)-Cl(4)	89.06(2)
Cl(1)-Re(1)-Cl(2)	91.95(3)	Cl(3)-Re(1)-Cl(5)	175.94(2)
Cl(1)-Re(1)-Cl(3)	91.77(3)	Cl(4)-Re(1)-Cl(5)	90.20(2)
Cl(1)-Re(1)-Cl(4)	92.87(3)		

Copper environment

Cu(1)-O(1)	1.959(2)	Cu(1)-N(2)	2.477(2)
Cu(1)-O(2)	1.969(2)		
O(1)-Cu(1)-O(1a)	180.00(1)	O(2)-Cu(1)-N(2)	92.82(7)
O(1)-Cu(1)-O(2)	91.05(7)	O(2)-Cu(1)-N(2a)	87.18(7)
O(1)-Cu(1)-O(2a)	88.95(7)	O(1a)-Cu(1)-N(2a)	85.54(7)
O(2)-Cu(1)-O(2a)	180.00(1)	O(1)-Cu(1)-N(2a)	94.46(7)
O(1a)-Cu(1)-N(2)	94.46(7)	N(2)-Cu(1)-N(2a)	180.00(8)
O(1)-Cu(1)-N(2)	85.54(7)		

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

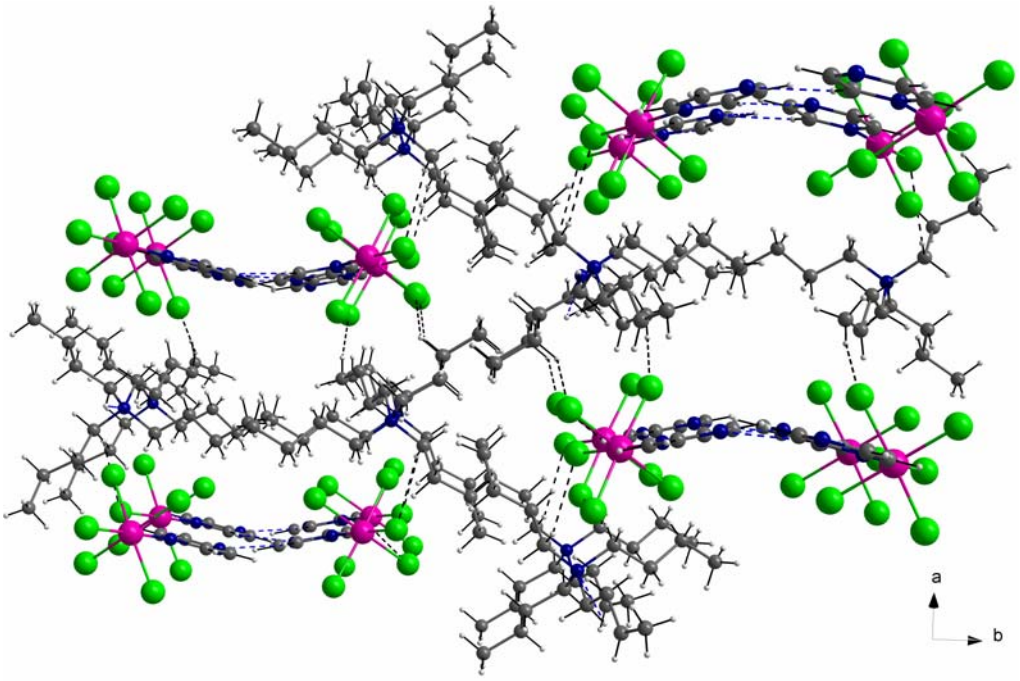

Figure S1 Perspective view along the *c* axis of the packing of **1** showing the weak Cl···H-C contacts (dashed lines) between $[ReCl_5(pyz)]^-$ anions and NBu_4^+ cations.

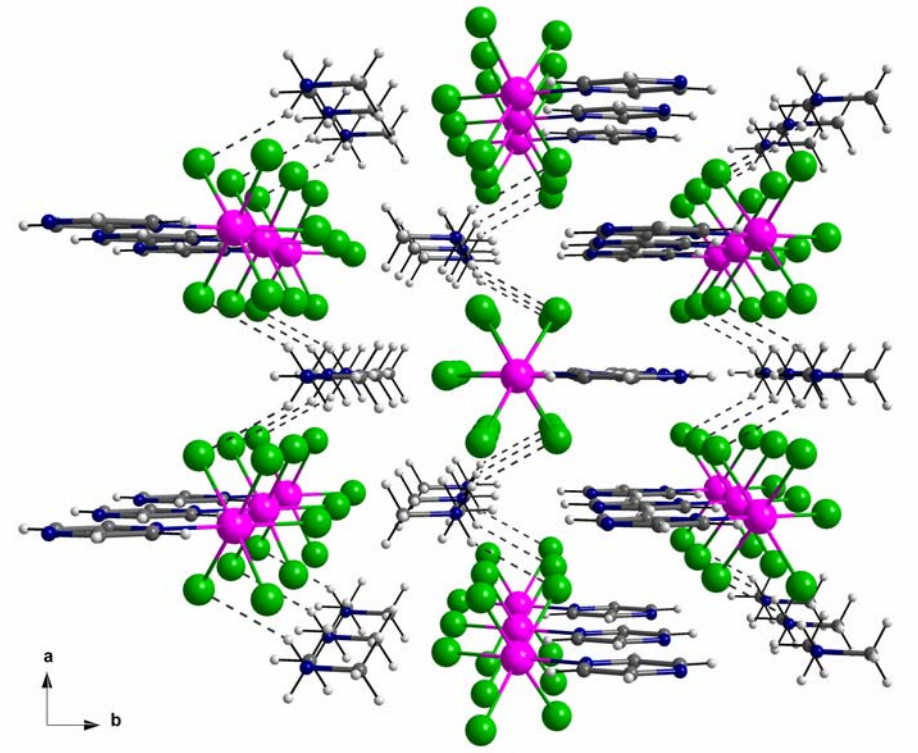

Figure S2 Perspective view along the *c* axis of the packing of **2** showing the hydrogen bonds (dashed lines) between $[ReCl_5(pyz)]^-$ anions and $NH_2Me_2^+$ cations.

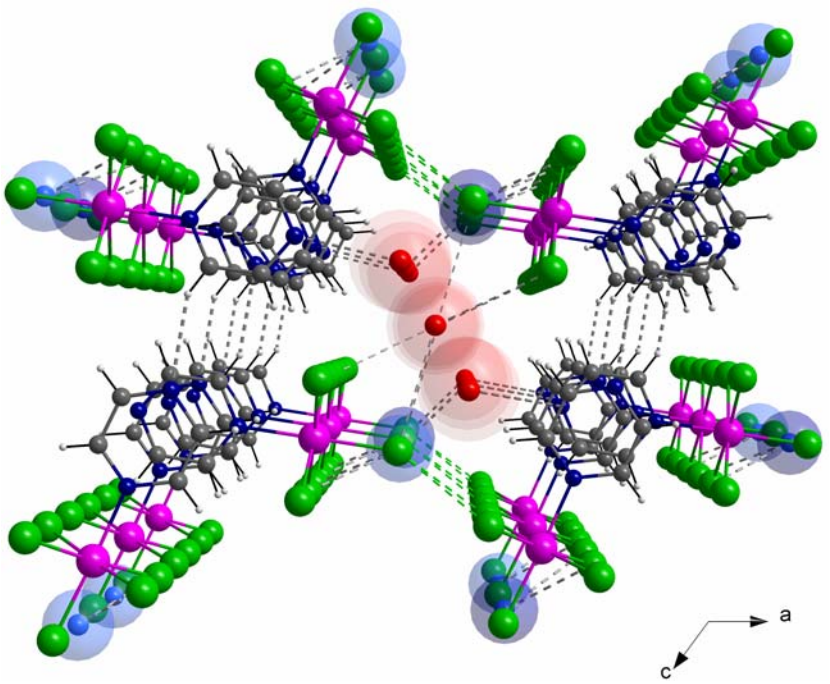

Figure S3 Perspective view along the *b* axis of a packing fragment of **3**, showing the channel in which crystallization water molecules are hosted. Ammonium cations and water molecules are evidenced with a semi-trasparent space-filling model (hydrogen atoms on them are not defined). Cl···Cl contacts, CH···N interactions and hydrogen bonds involving $[ReCl_5(pyz)]^-$ anions, NH_4^+ cations and water molecules are depicted as dashed lines.

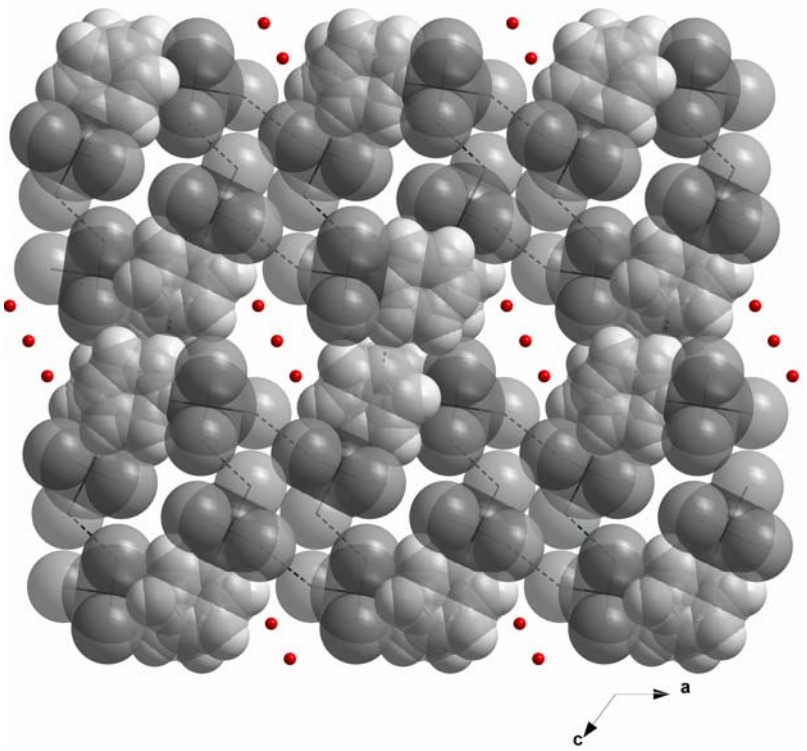

Figure S4 A space-filling view down the crystallographic *b* direction of the 3D supramolecular open-channel network including crystallization water molecules (small red balls) in complex **3**.

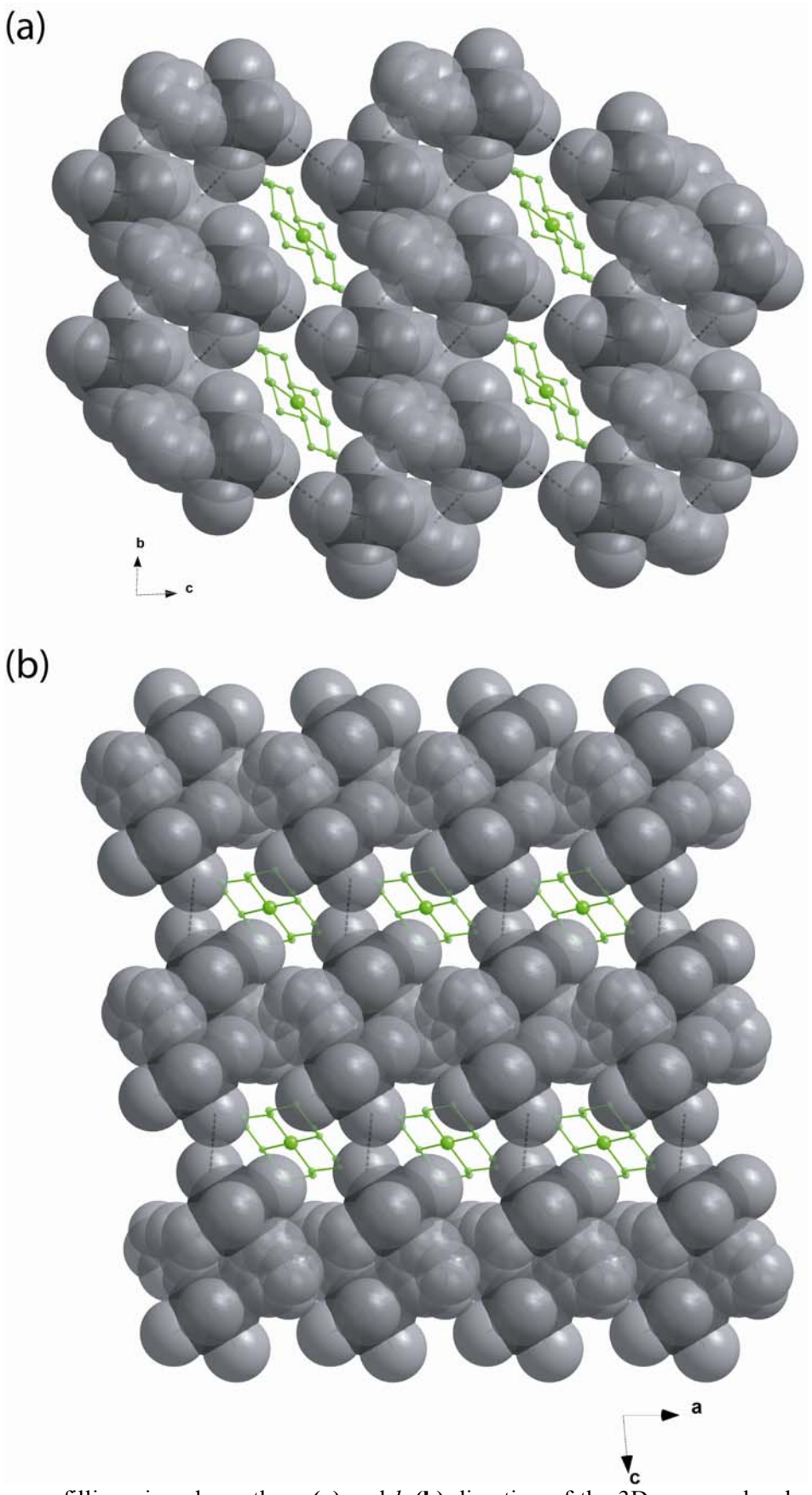

Figure S5 A space-filling view down the *a* **(a)** and *b* **(b)** direction of the 3D supramolecular open-channel network including $[Ni(cyclam)]^{2+}$ cations in complex **4**. Hydrogen atoms have been omitted for clearity.

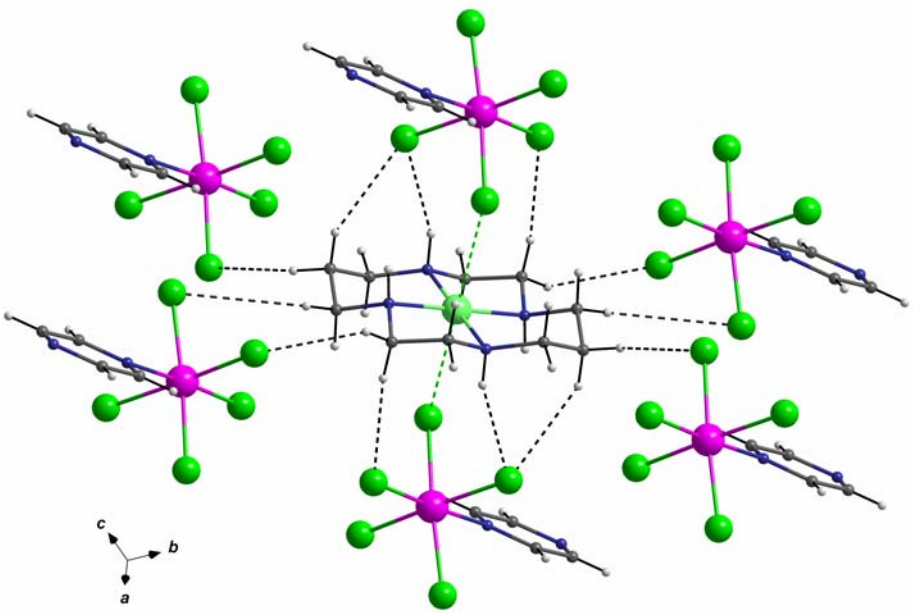

Figure S6 Weak Cl···H-C contacts (dashed lines) between $[Ni(cyclam)]^{2+}$ cations and $[ReCl_5(pyz)]^-$ anions in **4**.