Electronic Supplementary Information

A combined experimental and computational study on supramolecular assemblies in hetero-tetranuclear nickel(II)-cadmium(II) complexes with N_2O_4 donor compartmental Schiff bases

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Structure description of complex 1 (Unit B)

The molecular structure of unit **B** (Fig. S1) is built from isolated heteronuclear molecules of $[(CH_3CO_2)_2Ni_2(L^1)_2Cd_2(NCS)_2]$, in which both nickel(II) centres are hexacoordinated. H_2L^1 is a potential octadentate compartmental Schiff base with inner N_2O_2 and outer O_4 compartments. Nickel(II) centres occupy the inner N_2O_2 cavities while each cadmium(II) resides in the outer O_4 compartments. Both nickel(II) centres, [Ni(3) and Ni(4)], have pseudo octahedral geometries. Each nickel(II) centre is attached with two imine nitrogen atoms, [N(7) and N(8) for Ni(3); N(9) and N(10) for Ni(4)] and two phenoxo oxygen atoms, [O(13) and O(14) for Ni(3); O(17) and O(18) for Ni(4)] of the deprotonated Schiff base $(L^1)^{2-}$ constitute the equatorial plane. The fifth coordination site of each nickel centre is occupied by another phenoxo oxygen atom, [O(18) for Ni(3) and O(13) for Ni(4)], from the second deprotonated Schiff base. The octahedral geometries around both nickel(II) centres are fulfilled by the coordination of two oxygen atoms [O(22) for Ni(3); which bridges between Ni(3) and Cd(3) whereas O(24) for Ni(4); which bridges between

Ni(4) and Cd(4)] from two bridging acetates. For Ni(3) centre, the deviation of the coordinating atoms, O(13), O(14), N(8) and N(7) in the basal plane from the mean plane passing through them are -0.005(6), 0.013(6), -0.005(8), 0.013(9) Å respectively. The deviation of Ni(3) from the same plane is -0.017(13) Å. For Ni(4) centre, the deviation of the coordinating atoms O(17), O(18), N(9) and N(10) in the basal plane from the mean plane passing through them are -0.020(6), 0.007(6), -0.019(8), 0.007(8) Å respectively. The deviation of Ni(4) from the same plane is 0.0250(13) Å.

Each cadmium(II) centre is heptacoordinated. Each cadmium(II) resides in outer O_4 compartments being coordinated by two phenoxo [O(13) and O(14) for Cd(3); O(17) and O(18) for Cd(4)] and two methoxo oxygen atoms [O(15) and O(16)for Cd(3); O(19) and O(20) for Cd(4)]. The fifth coordination sites in each cadmium(II) is occupied by two terminal N-bonded thiocyanates [N(12) for Cd(3) and N(11) for Cd(4)]. Two phenoxo oxygen atoms [O(17) for Cd(3) and O(14) for Cd(4)] coordinate both cadmium(II) centres axially to complete its sixth coordination. The pentagonal bipyramidal geometry around each cadmium(II) is completed by the coordination of oxygen atoms [O(21) for Cd(3) and O(23) for Cd(4)] of bridging acetate groups.

Cadmium(II) and nickel(II) centres in the cubane reside in identical environment. Within the cubane unit Cd(3)-Ni(3), Ni(4)-Cd(4), Ni(4)-Ni(3) distances are significantly shorter (~3.316Å) compared to Cd(3)-Ni(4), Cd(4)-Ni(3) distances (~3.44Å), whereas the Cd(3)-Cd(4) distance is ~3.69Å. Thus the complex may be classified as a cubane with three short, two intermediate and one long Cd-Cd distances. The cubane core consist of two nickel(II) and two cadmium(II) centres which are bridged by phenoxo oxygen. The cubane core has six faces. The Cd_2O_2 face is opposite of Ni_2O_2 face. The bridging angles M-O-M (M = metal) are comparable.

The saturated six membered chelate rings [Ni(3)–N(7)–C(55)–C(54)–C(53)–N(8)] and [Ni(4)–N(9)–C(75)–C(76)–C(77)–N(10)] have envelope conformations with puckering parameters q = 0.507(14) Å; θ = 37.1(12)°; ϕ = 181(2)° and q = 0.530(14) Å; θ = 37.8(12)°; ϕ = 175(2)° respectively.

Table S1: Selected bond lengths (Å) for complex **1** (unit **B**).

Cd(3)-N(12)	2.199(11)	Cd(4)-N(11)	2.165(12)
Cd(3)-O(21)	2.214(8)	Ni(3)-O(13)	2.090(7)
Cd(3)-O(14)	2.407(6)	Ni(3)-N(8)	2.055(9)
Cd(3)-O(15)	2.560(7)	Ni(3)-N(7)	2.048(9)
Cd(3)-O(13)	2.354(7)	Ni(3)-O(22)	2.086(8)
Cd(3)-O(17)	2.286(6)	Ni(3)-O(14)	2.053(7)
Cd(3)-O(16)	2.518(8)	Ni(3)-O(18)	2.176(6)
Cd(4)-O(19)	2.551(9)	Ni(4)-O(18)	2.072(7)
Cd(4)-O(18)	2.370(7)	Ni(4)-N(10)	2.052(9)
Cd(4)-O(17)	2.397(6)	Ni(4)-O(24)	2.056(8)
Cd(4)-O(14)	2.323(6)	Ni(4)-N(9)	2.048(9)
Cd(4)-O(20)	2.567(7)	Ni(4)-O(17)	2.069(7)
Cd(4)-O(23)	2.221(8)	Ni(4)-O(13)	2.184(6)

Table S2: Selected bond angles (°) for complexes **1** (unit **A**) and **2**.

Complex	**1**	**2**	**Complex**	**1**	**2**
(1)-Cd(1)-O(2)	74.6(2)	72.46(12)	O(5)-Ni(2)-N(4)	176.0(3)	---
O(1)-Cd(1)-O(3)	63.7(2)	65.41(11)	O(1)-Ni(2)-O(11)	166.4(3)	---
O(1)-Cd(1)-O(4)	138.4(3)	137.43(11)	O(1)-Ni(2)-N(3)	95.1(3)	---
O(2)-Cd(1)-O(3)	138.1(2)	137.57(12)	O(1)-Ni(2)-N(4)	101.3(3)	---
O(2)-Cd(1)-O(4)	63.8(3)	64.99(12)	O(5)-Ni(2)-O(6)	88.0(3)	---

O(3)-Cd(1)-O(4)	157.5(3)	157.03(12)	O(5)-Ni(2)-O(11)	91.0(3)	---
O(6)-Cd(2)-O(7)	139.0(3)	73.62(9)	O(5)-Ni(2)-N(3)	89.6(3)	---
O(6)-Cd(2)-O(8)	64.0(3)	66.33(10)	O(1)-Ni(2)-O(5)	77.8(2)	---
O(7)-Cd(2)-O(8)	156.0(3)	138.73(11)	O(1)-Ni(2)-O(6)	82.9(3)	---
O(1)-Ni(1)-N(1)	89.0(4)	89.48(16)	O(6)-Ni(2)-N(4)	87.9(3)	---
O(1)-Ni(1)-N(2)	175.9(3)	172.53(15)	O(6)-Ni(2)-N(3)	177.1(3)	---
O(2)-Ni(1)-N(1)	176.5(4)	170.74(17)	N(3)-Ni(2)-N(4)	94.5(4)	---
O(2)-Ni(1)-N(2)	88.1(3)	91.22(16)	O(11)-Ni(2)-N(3)	92.3(4)	---
N(1)-Ni(1)-N(2)	94.9(4)	97.8(2)	O(11)-Ni(2)-N(4)	89.4(3)	---
O(6)-Ni(2)-O(11)	89.3(3)	89.05(17)	O(1)-Cd(1)-N(6)	---	107.2(15)
O(1)-Cd(1)-O(6)	73.8(2)	---	O(1)-Cd(1)-N(7)	---	120.71(16)
O(1)-Cd(1)-O(9)	87.0(3)	---	O(2)-Cd(1)-N(6)	---	109.82(17)
O(1)-Cd(1)-N(5)	140.1(3)	---	O(2)-Cd(1)-N(7)	---	118.54(17)
O(2)-Cd(1)-O(6)	75.3(2)	---	O(3)-Cd(1)-N(6)	---	87.72(17)
O(2)-Cd(1)-O(9)	83.7(3)	---	O(3)-Cd(1)-N(7)	---	80.85(17)
O(2)-Cd(1)-N(5)	143.6(3)	---	O(4)-Cd(1)-N(6)	---	86.44(16)
O(3)-Cd(1)-O(6)	96.0(2)	---	O(4)-Cd(1)-N(7)	---	82.64(17)
O(3)-Cd(1)-O(9)	90.1(3)	---	N(6)-Cd(1)-N(7)	---	119(2)
O(3)-Cd(1)-N(5)	78(3)	---	O(6)-Cd(2)-O(9)	---	137.58(10)
O(4)-Cd(1)-O(6)	95.9(3)	---	O(6)-Cd(2)-N(10)	---	107.08(14)
O(4)-Cd(1)-O(9)	87.4(4)	---	O(7)-Cd(2)-O(9)	---	63.96(10)
O(4)-Cd(1)-N(5)	80.9(4)	---	O(7)-Cd(2)-N(10)	---	110.56(14)
O(6)-Cd(1)-O(9)	154.4(3)	---	O(8)-Cd(2)-O(9)	---	154.9(11)
O(6)-Cd(1)-N(5)	101.1(4)	---	O(8)-Cd(2)-N(10)	---	90.78(14)
O(9)-Cd(1)-N(5)	104.4(4)	---	O(9)-Cd(2)-N(10)	---	88.04(13)
O(2)-Cd(2)-O(5)	73.6(2)	---	S(7)-Cd(2)-O(6)	---	119(8)
O(2)-Cd(2)-O(6)	75.3(3)	---	S(7)-Cd(2)-O(7)	---	101.65(8)
O(2)-Cd(2)-O(7)	95.3(2)	---	S(7)-Cd(2)-O(8)	---	89.65(8)
O(2)-Cd(2)-O(8)	98.4(3)	---	S(7)-Cd(2)-O(9)	---	72.05(8)
O(2)-Cd(2)-O(12)	154.6(3)	---	S(7)-Cd(2)-N(10)	---	129.36(13)

O(2)-Cd(2)-N(6)	100.6(4)	---	O(1)-Ni(1)-O(2)	---	81.59(11)
O(5)-Cd(2)-O(6)	74.6(2)	---	O(1)-Ni(1)-O(5)	---	90.90(11)
O(5)-Cd(2)-O(7)	64.0(2)	---	O(1)-Ni(1)-N(5)	---	92.67(14)
O(5)-Cd(2)-O(8)	139.1(3)	---	O(2)-Ni(1)-O(5)	---	89.66(13)
O(5)-Cd(2)-O(12)	86.8(3)	---	O(2)-Ni(1)-N(5)	---	88.90(16)
O(5)-Cd(2)-N(6)	140.6(4)	---	O(5)-Ni(1)-N(1)	---	92.94(19)
O(6)-Cd(2)-O(12)	84.0(3)	---	O(5)-Ni(1)-N(2)	---	86.98(14)
O(6)-Cd(2)-N(6)	142.9(4)	---	O(5)-Ni(1)-N(5)	---	175.91(15)
O(7)-Cd(2)-O(12)	90.3(3)	---	N(1)-Ni(1)-N(5)	---	89.1(2)
O(7)-Cd(2)-N(6)	78.2(3)	---	N(2)-Ni(1)-N(5)	---	89.27(17)
O(8)-Cd(2)-O(12)	85.7(3)	---	O(6)-Ni(2)-O(7)	---	83.07(10)
O(8)-Cd(2)-N(6)	79.9(4)	---	O(6)-Ni(2)-O(10)	---	92.48(13)
O(12)-Cd(2)-N(6)	104.9(4)	---	O(6)-Ni(2)-N(8)	---	89.88(13)
O(1)-Ni(1)-O(5)	77.2(2)	---	O(6)-Ni(2)-N(9)	---	172.35(14)
O(1)-Ni(1)-O(10)	91.2(3)	---	O(7)-Ni(2)-O(10)	---	89.33(12)
O(2)-Ni(1)-O(5)	82.1(3)	---	O(7)-Ni(2)-O(11)	---	90.78(17)
O(2)-Ni(1)-O(10)	89.1(3)	---	O(7)-Ni(2)-N(8)	---	172.94(13)
O(1)-Ni(1)-O(2)	88.1(3)	---	O(7)-Ni(2)-N(9)	---	89.74(13)
O(5)-Ni(1)-O(10)	165.6(3)	---	O(10)-Ni(2)-O(11)	---	178.47(17)
O(5)-Ni(1)-N(1)	95.7(3)	---	O(10)-Ni(2)-N(8)	---	91.05(15)
O(5)-Ni(1)-N(2)	101.2(3)	---	O(10)-Ni(2)-N(9)	---	89.98(15)
O(10)-Ni(1)-N(1)	92.5(4)	---	O(11)-Ni(2)-N(8)	---	89.03(18)
O(10)-Ni(1)-N(2)	89.9(3)	---	O(11)-Ni(2)-N(9)	---	88.49(18)
N(1)-Ni(1)-N(2)	95.0(4)	---	N(8)-Ni(2)-N(9)	---	97.31(16)

Table S3: Selected bond angles (°) for complex **1** (unit **B**).

O(14)-Cd(3)-O(16)	63.8(3)	O(18)-Cd(4)-N(11)	141.0(4)
O(14)-Cd(3)-O(17)	75.8(2)	O(19)-Cd(4)-O(20)	156.8(3)
O(14)-Cd(3)-O(21)	83.2(3)	O(19)-Cd(4)-O(23)	86.8(4)
O(14)-Cd(3)-N(12)	143.4(3)	O(19)-Cd(4)-N(11)	79.4(4)
O(15)-Cd(3)-O(16)	157.7(3)	O(20)-Cd(4)-O(23)	90.5(3)
O(15)-Cd(3)-O(17)	95.7(2)	O(13)-Ni(3)-O(14)	88.1(3)
O(15)-Cd(3)-O(21)	90.3(3)	O(14)-Ni(3)-N(7)	177.3(3)
O(15)-Cd(3)-N(12)	78.6(3)	O(13)-Ni(3)-O(18)	77.2(2)
O(16)-Cd(3)-O(17)	96.5(3)	O(13)-Ni(3)-O(22)	90.5(3)
O(16)-Cd(3)-O(21)	86.8(3)	O(13)-Ni(3)-N(7)	89.7(4)
O(16)-Cd(3)-N(12)	80.9(4)	O(13)-Ni(3)-N(8)	176.0(3)
O(17)-Cd(3)-O(21)	154.7(3)	O(14)-Ni(3)-O(18)	82.8(3)
O(17)-Cd(3)-N(12)	100.2(4)	O(14)-Ni(3)-O(22)	88.9(3)
O(21)-Cd(3)-N(12)	105.2(4)	N(7)-Ni(3)-N(8)	94.3(4)
O(13)-Cd(3)-O(16)	138.2(3)	O(18)-Ni(3)-N(7)	95.1(3)
O(13)-Cd(3)-O(17)	74.5(2)	O(14)-Ni(3)-N(8)	87.9(3)
O(13)-Cd(3)-O(21)	86.5(3)	O(18)-Ni(3)-O(22)	165.3(3)
O(13)-Cd(3)-N(12)	140.5(3)	O(22)-Ni(3)-N(8)	90.0(3)
O(14)-Cd(3)-O(15)	137.7(2)	O(18)-Ni(3)-N(8)	101.7(3)
O(13)-Cd(3)-O(14)	74.5(2)	O(22)-Ni(3)-N(7)	92.8(3)
O(13)-Cd(3)-O(15)	63.5(2)	O(13)-Ni(4)-O(17)	82.6(3)
O(14)-Cd(4)-N(11)	100.0(4)	O(17)-Ni(4)-N(9)	176.7(3)
O(17)-Cd(4)-O(20)	138.6(2)	O(13)-Ni(4)-O(18)	77.4(2)
O(17)-Cd(4)-O(23)	83.9(3)	O(13)-Ni(4)-O(24)	166.8(3)
O(17)-Cd(4)-N(11)	141.8(4)	O(13)-Ni(4)-N(9)	94.5(3)
O(18)-Cd(4)-O(19)	138.9(3)	O(13)-Ni(4)-N(10)	101.2(3)
O(18)-Cd(4)-O(20)	63.8(2)	O(17)-Ni(4)-O(18)	88.9(3)
O(17)-Cd(4)-O(18)	75(2)	O(17)-Ni(4)-O(24)	89.4(3)

O(17)-Cd(4)-O(19)	64.0(3)	O(24)-Ni(4)-N(10)	88.9(4)
O(14)-Cd(4)-O(17)	75.3(2)	N(9)-Ni(4)-N(10)	94.8(4)
O(14)-Cd(4)-O(18)	73.2(2)	O(18)-Ni(4)-O(24)	92.0(3)
O(14)-Cd(4)-O(19)	97.1(3)	O(18)-Ni(4)-N(9)	88.9(3)
O(14)-Cd(4)-O(20)	95.2(3)	O(17)-Ni(4)-N(10)	87.3(3)
O(14)-Cd(4)-O(23)	154.3(3)	O(24)-Ni(4)-N(9)	93.1(3)
O(23)-Cd(4)-N(11)	105.7(5)	O(18)-Ni(4)-N(10)	176.1(3)
O(20)-Cd(4)-N(11)	79.1(4)	O(24)-Ni(4)-N(9)	93.1(3)
O(18)-Cd(4)-O(23)	87.1(3)	O(18)-Ni(4)-N(10)	176.1(3)

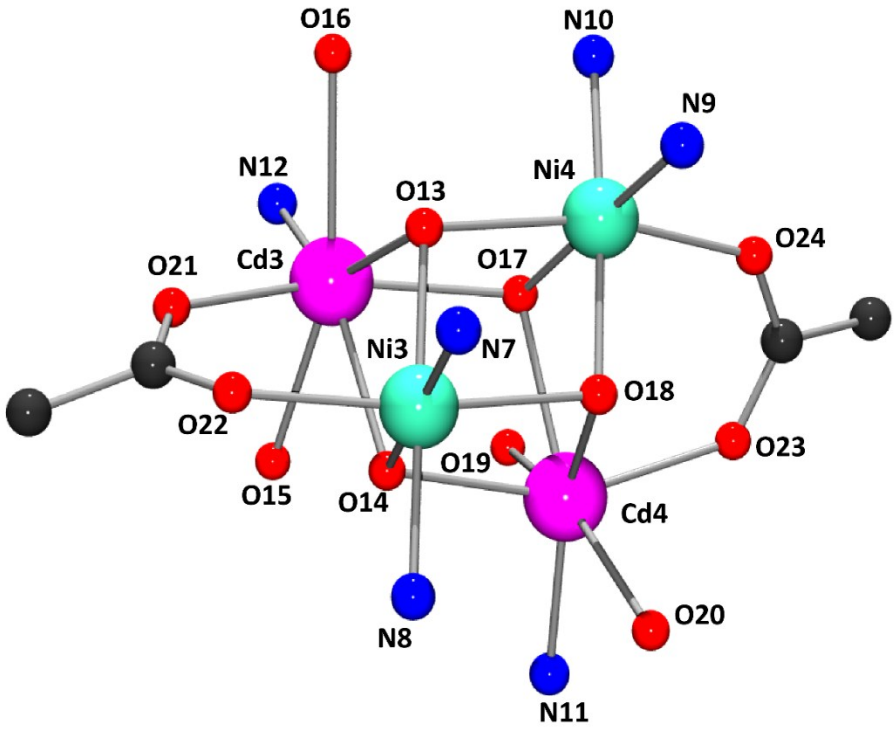

Fig. S1: Perspective view of $Cd_2Ni_2O_4$ cubane core of unit **B** along with coordinating atoms and bridging acetate ligands.

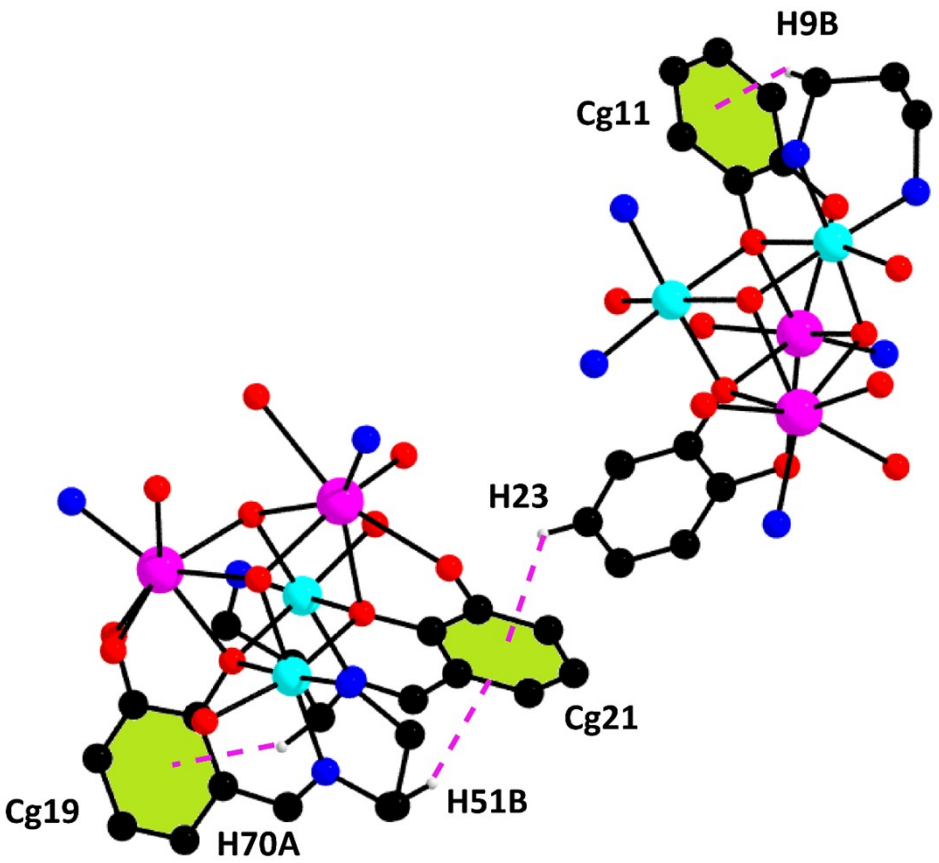

Fig. S2: Perspective view of C-H···π interactions of complex **1** with selective atom numbering scheme. Cubane core along with coordinating atoms, interacting hydrogens and π systems have been shown in the figure.

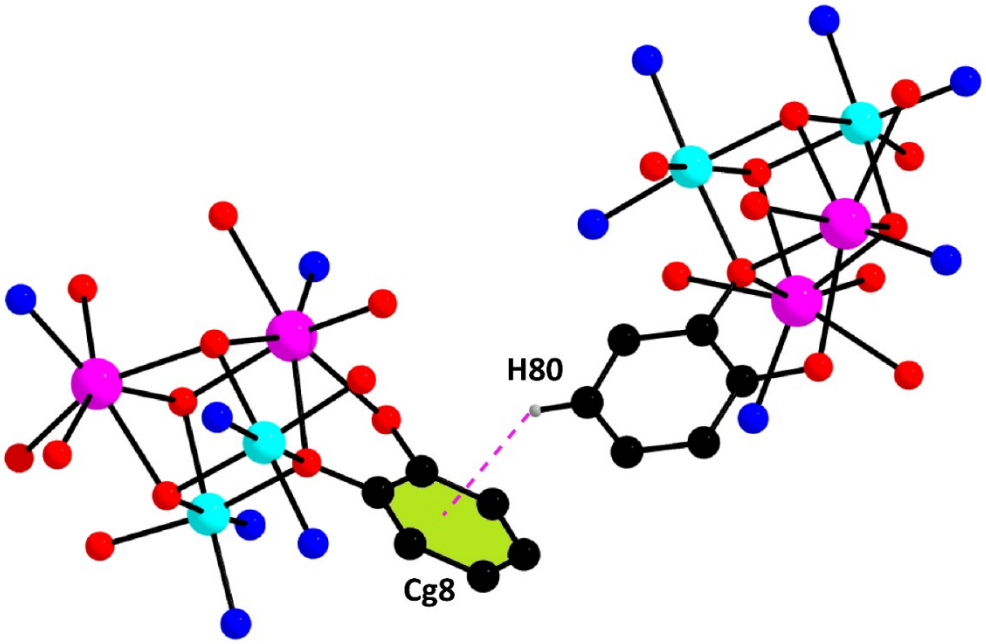

Fig. S3: Perspective view of the supra-molecular dimer formed by inter-molecular C-H···π interactions of complex **1** with selective atom numbering scheme. Cubane core along with coordinating atoms, interacting hydrogen and π system have been shown in the figure.

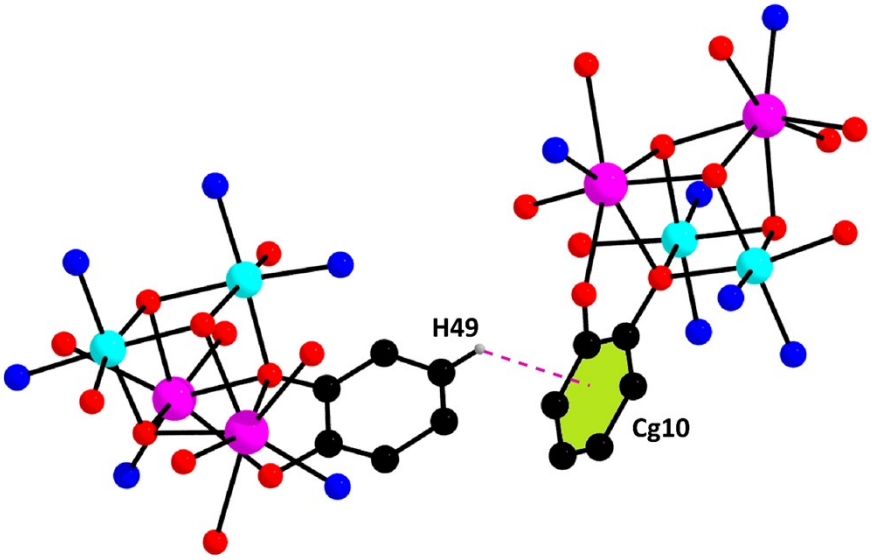

Fig. S4: Perspective view of the supra-molecular dimer formed by inter-molecular C-H···π interactions of complex **1** with selective atom numbering scheme. Cubane core along with coordinating atoms, interacting hydrogen and π system have been shown in the figure.

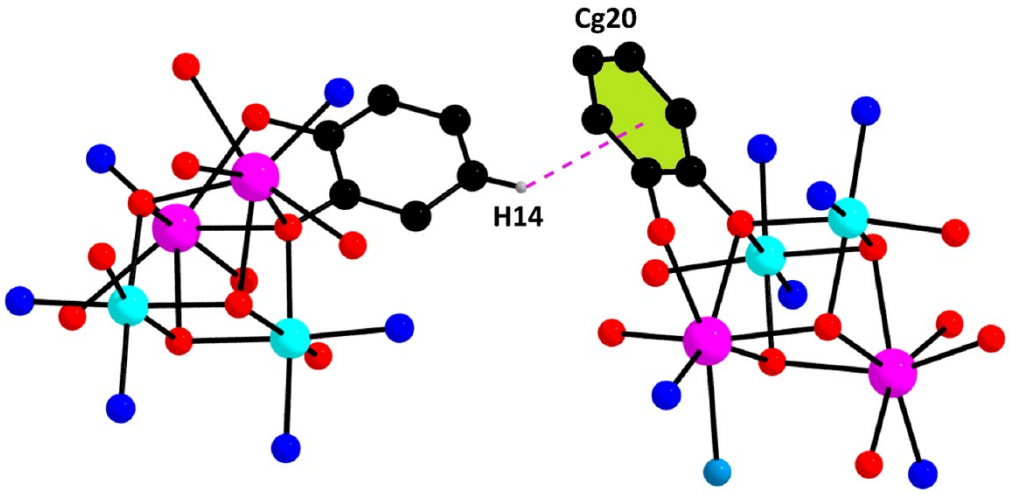

Fig. S5: Perspective view of the supra-molecular dimer formed by inter-molecular C-H···π interactions of complex **1** with selective atom numbering scheme. Cubane core along with coordinating atoms and interacting hydrogen, Cg are shown in the figure.

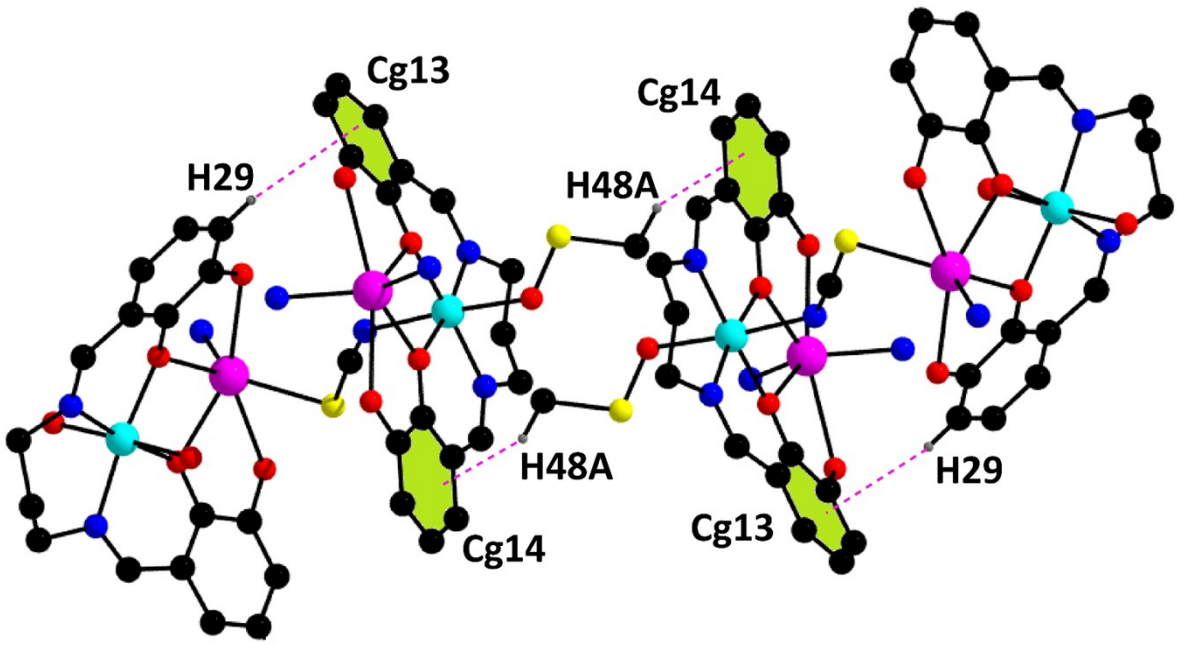

Fig. S6: Perspective view of the C-H···π interactions of complex **2** with selective atom numbering scheme. Hydrogen atoms, methyl and ethyl groups except the interacting ones have been omitted for clarity.

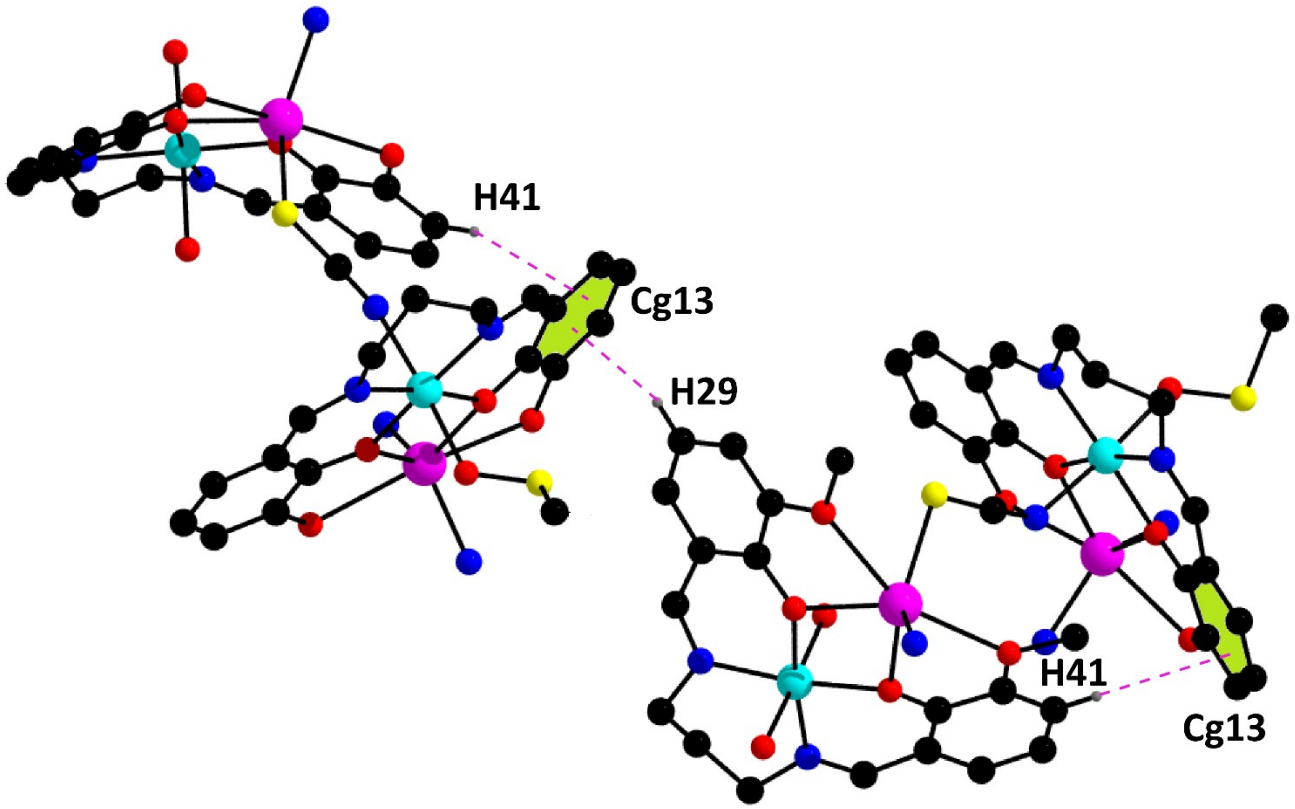

Fig. S7: Perspective view of dimer formed by C-H···π interactions of complex **2** with selective atom numbering scheme. Hydrogen atoms, methyl and ethyl groups except the interacting ones have been omitted for clarity.