Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Supramolecular Interactions Mediated Conformational Modulation of Flexible Linker Leading to Isolation of Metallo-Macrocycle in the Polyoxometalate Matrix: Hirshfeld surfaces and 2D finger print plots

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Contents

Section 1

Additional diagrams of crystal structure

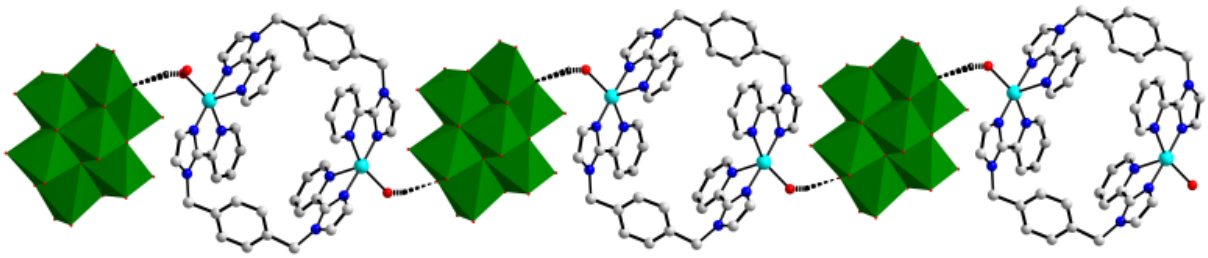


Fig. S1. 1D chain formed due to O-H…O interactions forming a 1D chain.

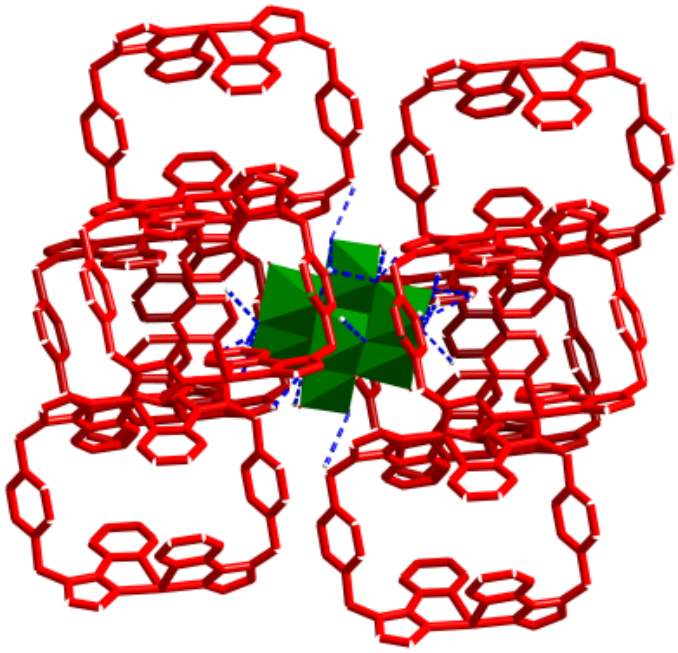


Fig. S2. Supramolecular interactions around the anion.

Section 2

Theoretical Calculations

a. Optimized geometries and energies of cis and trans conformations of 1,4-bpimb linker

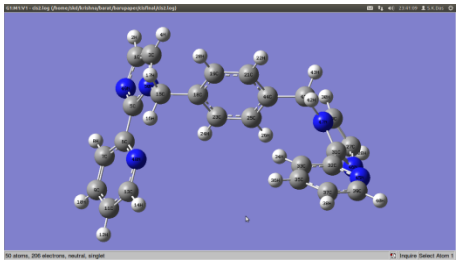
cis2.log (~/krishna/barat/barupaper/cisfinal) - VIM

skd@skd: ~ | cis2.log (~/krishna/barat/barupaper/cisfinal

```
                       1640.66  1668.52  1687.54  1689.98  1692.63
                       1724.16  1735.53  1737.30  1746.59  1765.86
                       1830.04  1840.63  1844.83  1866.70  1870.61
                       1874.29  1884.19  1897.32  1903.63  1933.29
                       1988.09  1995.64  2010.90  2029.39  2061.37
                       2067.87  2085.34  2089.40  2107.66  2118.22
                       2129.24  2145.81  2159.76  2172.01  2176.87
                       2223.94  2232.68  2235.24  2306.04  2315.51
                       2323.40  2339.35  2344.13  2379.77  4375.84
                       4399.57  4445.55  4511.86  4526.98  4528.80
                       4531.26  4553.61  4562.82  4567.16  4571.93
                       4588.83  4592.55  4597.60  4598.36  4629.85
                       4654.75  4656.92  4693.84  4696.78

Zero-point correction=                           0.397187 (Hartree/Particle)
Thermal correction to Energy=                    0.420990
Thermal correction to Enthalpy=                  0.421935
Thermal correction to Gibbs Free Energy=         0.336960
Sum of electronic and zero-point Energies=          -1255.017264
Sum of electronic and thermal Energies=             -1254.993461
Sum of electronic and thermal Enthalpies=           -1254.992516
Sum of electronic and thermal Free Energies=        -1255.077491

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  264.175            93.120           178.844
Electronic               0.000             0.000             0.000
Translational            0.889             2.981            43.791
Rotational               0.889             2.981            36.831
Vibrational            262.398            87.158            98.221
Vibration     1          0.593             1.987             8.767
Vibration     2          0.593             1.987             7.775
Vibration     3          0.593             1.986             7.229
Vibration     4          0.593             1.985             6.298
Vibration     5          0.594             1.983             5.539
Vibration     6          0.594             1.982             5.487
Vibration     7          0.595             1.980             5.068
Vibration     8          0.598             1.970             4.251
```



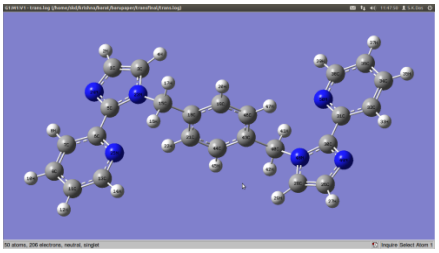
trans.log (~/krishna/barat/barupaper/transfinal) - VIM

skd@skd: ~ | trans.lo

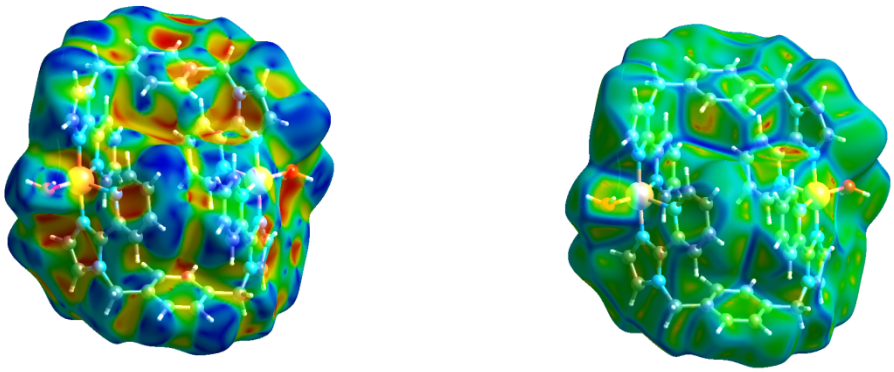
```
                       1638.75  1687.48  1687.49  1692.31  1692.67
                       1732.25  1736.53  1741.46  1751.99  1769.23
                       1832.92  1834.14  1866.26  1867.68  1870.51
                       1876.03  1883.16  1888.91  1918.80  1930.25
                       1988.42  1998.38  2027.79  2030.21  2060.02
                       2061.81  2088.46  2105.84  2105.89  2118.80
                       2120.32  2146.57  2146.96  2177.30  2177.88
                       2224.25  2232.02  2232.44  2305.45  2305.54
                       2323.89  2343.98  2344.00  2380.19  4396.70
                       4396.71  4498.36  4499.09  4530.34  4530.35
                       4539.60  4541.82  4565.67  4565.68  4579.80
                       4582.18  4596.65  4596.67  4630.82  4630.83
                       4656.05  4656.06  4697.69  4697.70

Zero-point correction=                           0.397540 (Hartree/Particle)
Thermal correction to Energy=                    0.421327
Thermal correction to Enthalpy=                  0.422271
Thermal correction to Gibbs Free Energy=         0.335464
Sum of electronic and zero-point Energies=          -1255.029234
Sum of electronic and thermal Energies=             -1255.005447
Sum of electronic and thermal Enthalpies=           -1255.004503
Sum of electronic and thermal Free Energies=        -1255.091310

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  264.387            92.988           182.700
Electronic               0.000             0.000             0.000
Translational            0.889             2.981            43.791
Rotational               0.889             2.981            36.895
Vibrational            262.609            87.027           102.013
Vibration     1          0.592             1.987            10.402
Vibration     2          0.593             1.987             8.374
Vibration     3          0.593             1.986             7.345
Vibration     4          0.593             1.986             6.853
Vibration     5          0.593             1.985             6.487
Vibration     6          0.593             1.985             6.083
Vibration     7          0.595             1.979             4.937
Vibration     8          0.597             1.971             4.328
```

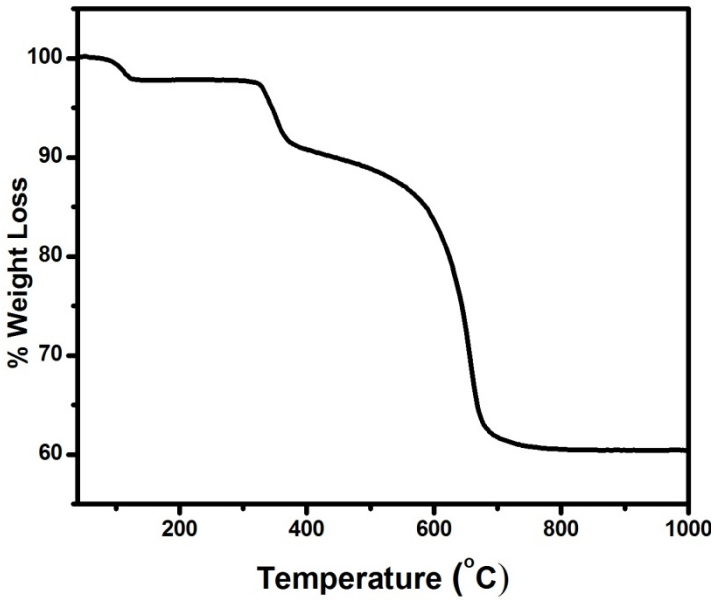


b. Hirshfeld surfaces mapped with shape index (left) and curvedness (right) for the title compound

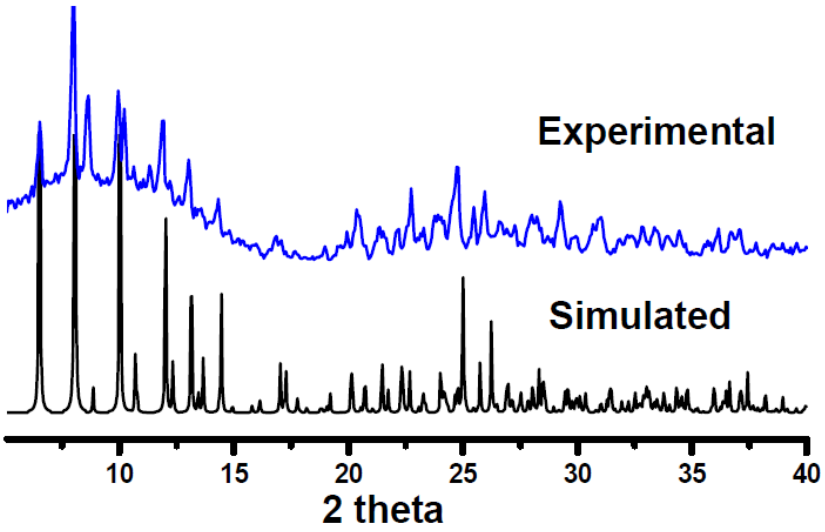


Section 3

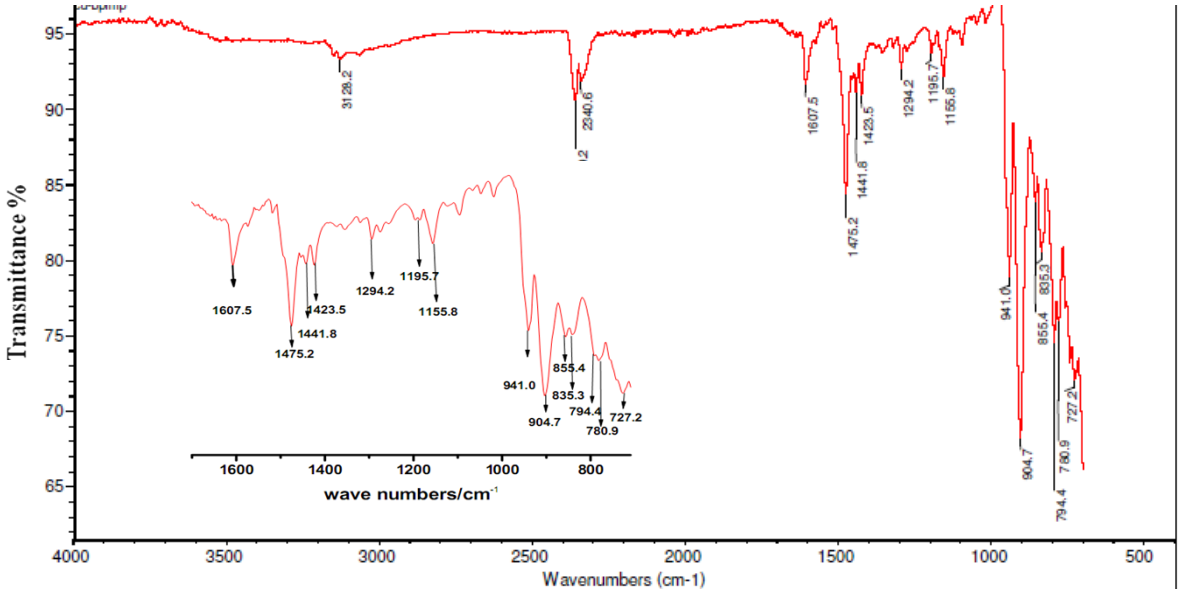
a. Thermogravimetric curve of $[Cu(1,4\text{-bpimb})(H_2O)]_2[Mo_8O_{26}]\cdot 4H_2O$



b. PXRD of $[Cu(1,4\text{-bpimb})(H_2O)]_2[Mo_8O_{26}]\cdot 4H_2O$



c. IR spectrum of $[Cu(1,4\text{-bpimb})(H_2O)]_2[Mo_8O_{26}]\cdot 4H_2O$



Section 4

Table 1. List of bond lengths in the octamolybdate anion and Cu(II) coordination sphere

Mo-O_t	Mo-O(μ_2)	Mo-O(μ_3)	Mo- O(μ_4)	Cu-N/ Cu-O
Mo(1)-O(1) 1.685(6)	Mo(1)-O(2) 1.740(6)	Mo(1)-O(3) 1.946(5)	Mo(1)-O(13) 2.131(5)	Cu(5)-N(1) 2.051(7)
Mo(2)-O(5) 1.698(6)	Mo(2)-O(6) 1.901(5)	Mo(1)-O(12) 1.946(6)	Mo(1)-O(13)$^{\#1}$ 2.377(5)	Cu(5)-N(2) 1.932(7)
Mo(2)-O(4) 1.711(6)	Mo(3)-O(9) 1.920(5)	Mo(2)-O(3) 1.973(6)	Mo(2)-O(13) 2.318(5)	Cu(5)-N(4) 2.197(7)
Mo(3)-O(10) 1.697(6)	Mo(4)-O(6) 1.898(5)	Mo(2)-O(12)$^{\#1}$ 2.348(6)	Mo(3)-O(13) 2.299(5)	Cu(5)-N(5) 1.963(8)
Mo(3)-O(11) 1.699(6)	Mo(4)-O(9) 1.925(6)	Mo(3)-O(12) 1.972(6)	Mo(4)-O(13) 2.493(5)	Cu(5)-O(16) 2.037(7)
Mo(4)-O(8) 1.687(6)	O(2)-Mo(4)$^{\#1}$ 2.274(6)	Mo(3)-O(3)$^{\#1}$ 2.357(6)		
Mo(4)-O(7) 1.701(6)				
#1 -x+1, -y+2, -z				

Table 2

Complete list of bond lengths and bond angles

C(1)-C(2)	1.328(13)		
C(1)-N(5)	1.356(11)	C(20)-C(21)	1.354(13)
C(2)-N(6)	1.377(12)	C(21)-C(22)	1.387(13)
C(3)-N(5)	1.313(11)	C(22)-N(1)	1.319(11)
C(3)-N(6)	1.338(10)	C(23)-N(3)	1.456(11)
C(3)-C(4)	1.498(12)	C(23)-C(24)	1.489(12)
C(4)-N(4)	1.340(11)	C(24)-C(14)#1	1.374(12)
C(4)-C(5)	1.377(12)	C(24)-C(12)#1	1.403(12)
C(5)-C(6)	1.401(12)	Cu(5)-N(2)	1.932(7)
C(6)-C(7)	1.378(12)	Cu(5)-N(5)	1.963(8)
C(7)-C(8)	1.391(12)	Cu(5)-O(16)	2.037(7)
C(8)-N(4)	1.319(11)	Cu(5)-N(1)	2.051(7)
C(9)-N(6)	1.463(11)	Cu(5)-N(4)	2.197(7)
C(9)-C(10)	1.512(13)	Mo(1)-O(1)	1.685(6)
C(10)-C(11)	1.368(12)	Mo(1)-O(2)	1.740(6)
C(10)-C(13)	1.402(12)	Mo(1)-O(3)	1.946(5)
C(11)-C(12)	1.379(12)	Mo(1)-O(12)	1.946(6)
C(12)-C(24)#1	1.403(12)	Mo(1)-O(13)	2.131(5)
C(13)-C(14)	1.390(12)	Mo(1)-O(13)#2	2.377(5)
C(14)-C(24)#1	1.374(12)	Mo(2)-O(5)	1.698(6)
C(15)-C(16)	1.345(12)	Mo(2)-O(4)	1.711(6)
C(15)-N(2)	1.365(10)	Mo(2)-O(6)	1.901(5)
C(16)-N(3)	1.365(10)	Mo(2)-O(3)	1.973(6)
C(17)-N(2)	1.321(11)	Mo(2)-O(13)	2.318(5)
C(17)-N(3)	1.357(11)	Mo(2)-O(12)#2	2.348(6)
C(17)-C(18)	1.462(12)	Mo(3)-O(10)	1.697(6)
C(18)-N(1)	1.367(11)	Mo(3)-O(11)	1.699(6)
C(18)-C(19)	1.375(12)	Mo(3)-O(9)	1.920(5)
C(19)-C(20)	1.376(12)	Mo(3)-O(12)	1.972(6)

Mo(3)-O(13)	2.299(5)
Mo(3)-O(3)#2	2.357(6)
Mo(4)-O(8)	1.687(6)
Mo(4)-O(7)	1.701(6)
Mo(4)-O(6)	1.898(5)
Mo(4)-O(9)	1.925(6)
Mo(4)-O(2)#2	2.274(6)
Mo(4)-O(13)	2.493(5)
O(2)-Mo(4)#2	2.274(6)
O(3)-Mo(3)#2	2.357(6)
O(12)-Mo(2)#2	2.348(6)
O(13)-Mo(1)#2	2.377(5)

C(2)-C(1)-N(5)	110.2(8)
C(1)-C(2)-N(6)	106.4(8)
N(5)-C(3)-N(6)	111.0(7)
N(5)-C(3)-C(4)	119.2(8)
N(6)-C(3)-C(4)	129.8(7)
N(4)-C(4)-C(5)	123.2(8)
N(4)-C(4)-C(3)	111.3(7)
C(5)-C(4)-C(3)	125.4(8)
C(4)-C(5)-C(6)	117.8(8)
C(7)-C(6)-C(5)	119.1(8)
C(6)-C(7)-C(8)	118.6(8)
N(4)-C(8)-C(7)	122.8(9)
N(6)-C(9)-C(10)	113.1(7)
C(11)-C(10)-C(13)	119.3(9)
C(11)-C(10)-C(9)	118.0(8)
C(13)-C(10)-C(9)	122.7(8)
C(10)-C(11)-C(12)	121.5(8)
C(11)-C(12)-C(24)#1	120.1(8)
C(14)-C(13)-C(10)	119.0(8)
C(24)#1-C(14)-C(13)	121.9(8)
C(16)-C(15)-N(2)	108.8(8)
C(15)-C(16)-N(3)	107.4(7)
N(2)-C(17)-N(3)	110.0(8)
N(2)-C(17)-C(18)	118.7(8)
N(3)-C(17)-C(18)	131.2(8)
N(1)-C(18)-C(19)	121.3(8)
N(1)-C(18)-C(17)	111.2(8)
C(19)-C(18)-C(17)	127.5(8)
C(18)-C(19)-C(20)	118.4(9)
C(21)-C(20)-C(19)	120.1(9)
C(20)-C(21)-C(22)	119.3(8)
N(1)-C(22)-C(21)	121.6(9)
O(10)-Mo(3)-O(9)	101.8(3)
O(11)-Mo(3)-O(9)	99.9(3)
O(10)-Mo(3)-O(12)	97.1(3)
O(11)-Mo(3)-O(12)	101.8(3)
O(9)-Mo(3)-O(12)	146.6(2)
O(10)-Mo(3)-O(13)	94.9(2)
O(11)-Mo(3)-O(13)	160.9(2)
O(9)-Mo(3)-O(13)	77.5(2)
O(12)-Mo(3)-O(13)	73.6(2)
O(10)-Mo(3)-O(3)#2	164.3(2)
O(11)-Mo(3)-O(3)#2	88.9(2)
N(3)-C(23)-C(24)	113.6(7)
C(14)#1-C(24)-C(12)#1	118.2(8)
C(14)#1-C(24)-C(23)	123.5(8)
C(12)#1-C(24)-C(23)	118.3(8)
N(2)-Cu(5)-N(5)	177.3(3)
N(2)-Cu(5)-O(16)	93.4(3)
N(5)-Cu(5)-O(16)	88.6(3)
N(2)-Cu(5)-N(1)	81.2(3)
N(5)-Cu(5)-N(1)	97.7(3)
O(16)-Cu(5)-N(1)	155.4(3)
N(2)-Cu(5)-N(4)	99.9(3)
N(5)-Cu(5)-N(4)	78.1(3)
O(16)-Cu(5)-N(4)	94.0(3)
N(1)-Cu(5)-N(4)	110.6(3)
O(1)-Mo(1)-O(2)	104.3(3)
O(1)-Mo(1)-O(3)	101.8(3)
O(2)-Mo(1)-O(3)	96.3(2)
O(1)-Mo(1)-O(12)	101.2(3)
O(2)-Mo(1)-O(12)	97.1(2)
O(3)-Mo(1)-O(12)	149.5(2)
O(1)-Mo(1)-O(13)	99.3(2)
O(2)-Mo(1)-O(13)	156.4(2)
O(3)-Mo(1)-O(13)	78.7(2)
O(12)-Mo(1)-O(13)	78.1(2)
O(1)-Mo(1)-O(13)#2	174.8(2)
O(2)-Mo(1)-O(13)#2	80.9(2)
O(3)-Mo(1)-O(13)#2	77.8(2)
O(12)-Mo(1)-O(13)#2	77.4(2)
O(13)-Mo(1)-O(13)#2	75.5(2)
O(5)-Mo(2)-O(4)	105.1(3)
O(5)-Mo(2)-O(6)	100.4(3)
O(4)-Mo(2)-O(6)	101.7(3)
O(5)-Mo(2)-O(3)	100.3(3)
O(4)-Mo(2)-O(3)	98.3(3)
O(6)-Mo(2)-O(3)	146.2(2)
O(5)-Mo(2)-O(13)	160.0(2)
O(4)-Mo(2)-O(13)	94.8(2)
O(6)-Mo(2)-O(13)	77.7(2)
O(3)-Mo(2)-O(13)	73.7(2)
O(5)-Mo(2)-O(12)#2	88.5(2)
O(4)-Mo(2)-O(12)#2	164.5(2)
O(6)-Mo(2)-O(12)#2	82.7(2)
O(3)-Mo(2)-O(12)#2	71.5(2)
O(13)-Mo(2)-O(12)#2	71.44(19)
O(10)-Mo(3)-O(11)	104.2(3)
O(9)-Mo(3)-O(3)#2	84.1(2)
O(12)-Mo(3)-O(3)#2	71.3(2)
O(13)-Mo(3)-O(3)#2	71.96(19)
O(8)-Mo(4)-O(7)	104.3(3)
O(8)-Mo(4)-O(6)	104.4(3)
O(7)-Mo(4)-O(6)	98.0(3)
O(8)-Mo(4)-O(9)	102.3(3)
O(7)-Mo(4)-O(9)	98.8(3)
O(6)-Mo(4)-O(9)	143.7(2)
O(8)-Mo(4)-O(2)#2	89.4(2)
O(7)-Mo(4)-O(2)#2	166.3(2)

O(6)-Mo(4)-O(2)#2	78.5(2)	Mo(1)-O(3)-Mo(3)#2	109.7(3)
O(9)-Mo(4)-O(2)#2	77.7(2)	Mo(2)-O(3)-Mo(3)#2	104.2(2)
O(8)-Mo(4)-O(13)	158.6(2)	Mo(4)-O(6)-Mo(2)	118.1(3)
O(7)-Mo(4)-O(13)	97.0(2)	Mo(3)-O(9)-Mo(4)	118.3(3)
O(6)-Mo(4)-O(13)	73.4(2)	Mo(1)-O(12)-Mo(3)	108.9(3)
O(9)-Mo(4)-O(13)	72.7(2)	Mo(1)-O(12)-Mo(2)#2	110.6(2)
O(2)#2-Mo(4)-O(13)	69.29(18)	Mo(3)-O(12)-Mo(2)#2	104.5(2)
C(22)-N(1)-C(18)	119.2(8)	Mo(1)-O(13)-Mo(3)	92.0(2)
C(22)-N(1)-Cu(5)	127.1(6)	Mo(1)-O(13)-Mo(2)	91.55(19)
C(18)-N(1)-Cu(5)	113.5(5)	Mo(3)-O(13)-Mo(2)	162.6(3)
C(17)-N(2)-C(15)	107.0(7)	Mo(1)-O(13)-Mo(1)#2	104.5(2)
C(17)-N(2)-Cu(5)	115.2(6)	Mo(3)-O(13)-Mo(1)#2	97.83(19)
C(15)-N(2)-Cu(5)	137.8(6)	Mo(2)-O(13)-Mo(1)#2	97.8(2)
C(17)-N(3)-C(16)	106.8(7)	Mo(1)-O(13)-Mo(4)	164.7(3)
C(17)-N(3)-C(23)	128.2(8)	Mo(3)-O(13)-Mo(4)	86.95(17)
C(16)-N(3)-C(23)	124.9(8)	Mo(2)-O(13)-Mo(4)	85.18(17)
Mo(1)-O(2)-Mo(4)#2	118.9(3)	Mo(1)#2-O(13)-Mo(4)	90.78(17)
Mo(1)-O(3)-Mo(2)	109.0(3)		

********** *******End**********