Supporting Information

Tetranuclear Mn^{II}, Co^{II}, Cu^{II} and Zn^{II} Grid Complexes of an Unsymmetrical Ditopic Ligand: Synthesis, Structure, Redox and Magnetic properties

Avinash Lakma,†,§ Sayed Muktar Hossain,†,§ Jan van Leusen,‡ Paul Kögerler*,‡ and Akhilesh Kumar Singh*,

†§These authors have equal contribution.

†School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Bhubaneswar 752 050.

‡ Institut für Anorganische Chemie, RWTH Aachen University, 52074 Aachen, Germany.

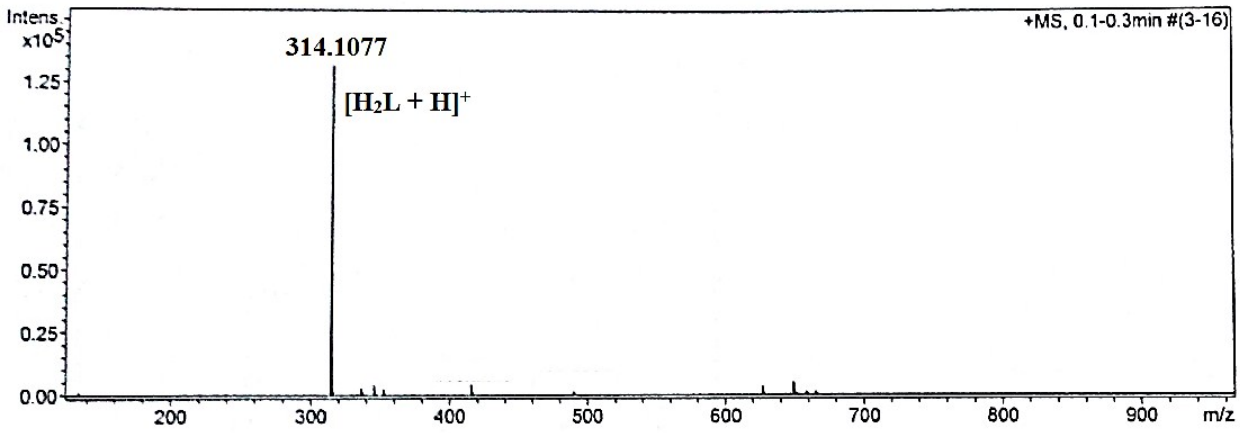

Fig. S1 ESI-MS spectrum of H_2L.

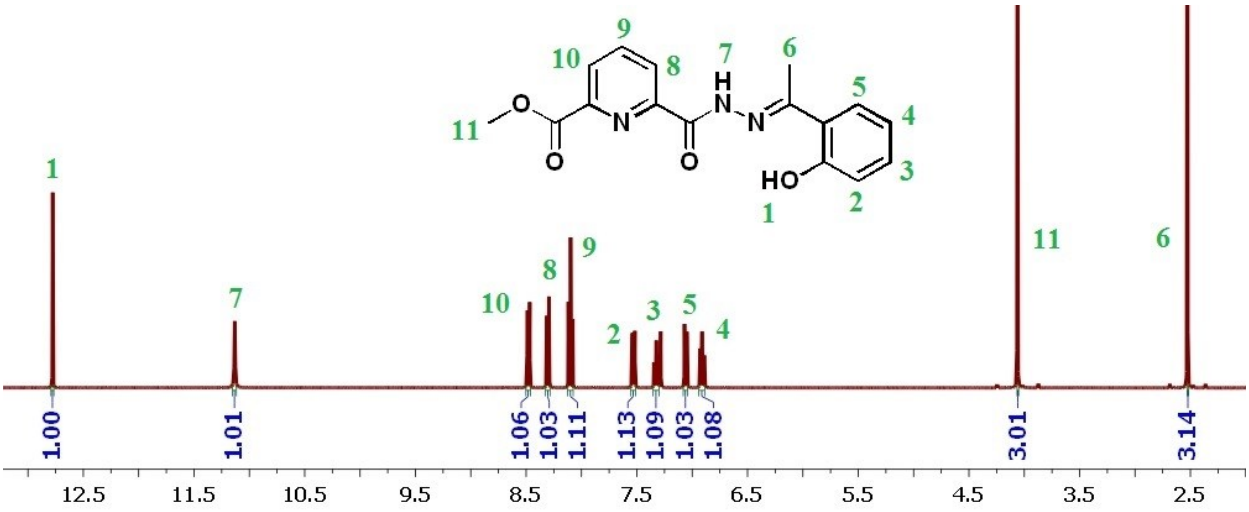

Fig. S2 ^{1}H NMR spectrum of H_2L in $CDCl_3$.

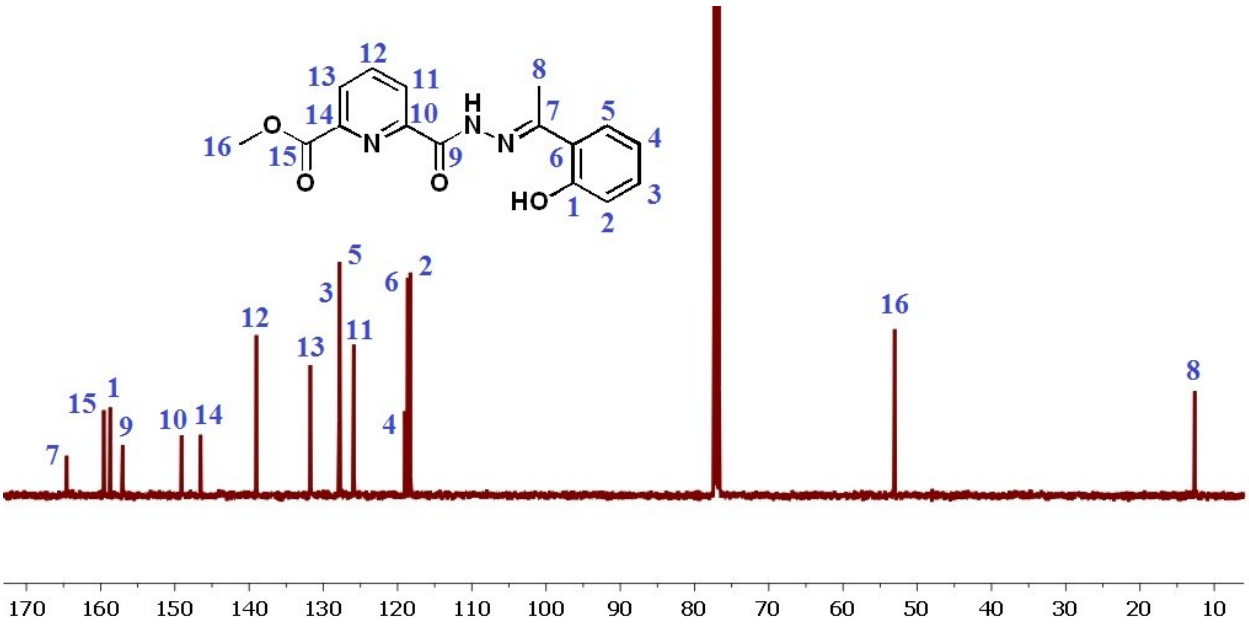

Fig. S3 ^{13}C NMR spectrum of H_2L in $CDCl_3$.

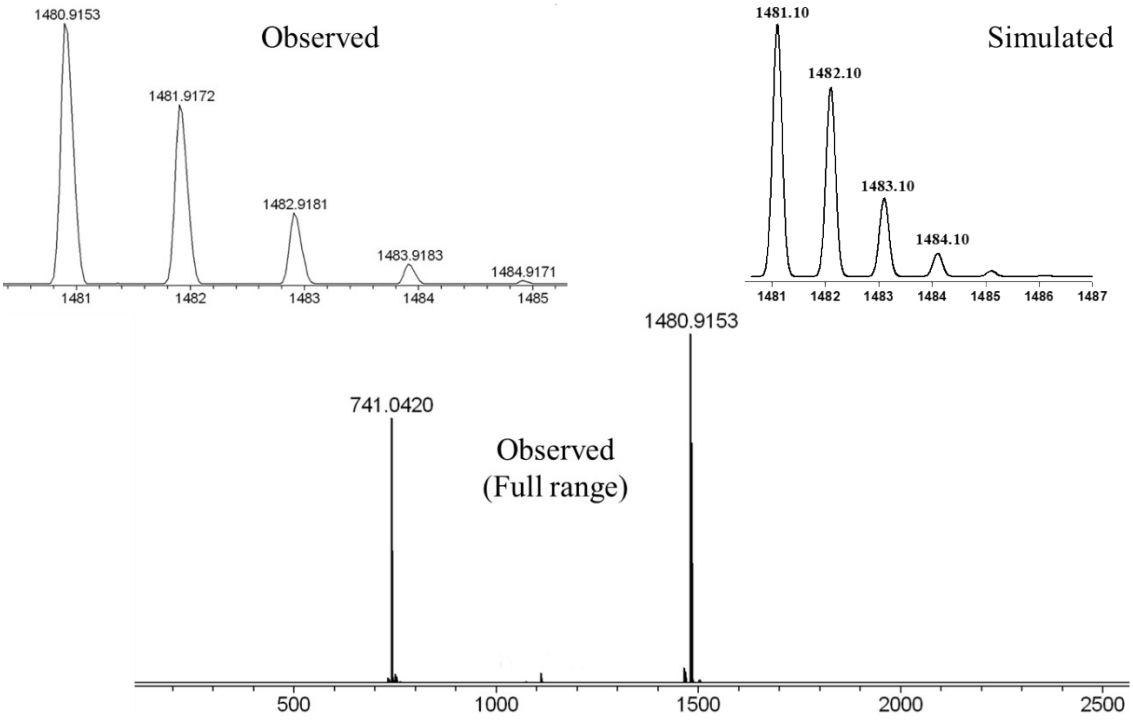

Fig. S4 Observed and simulated ESI-Mass spectra of Co_4-grid complex (**2**).

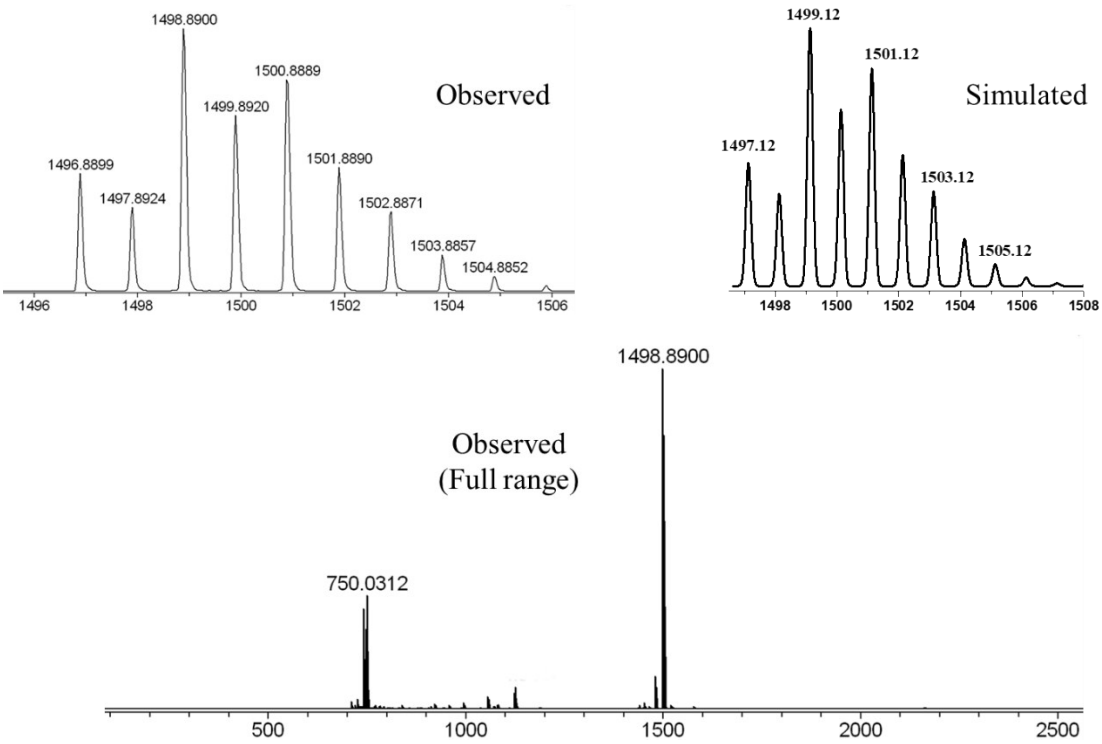

Fig. S5 Observed and simulated ESI-Mass spectra of Cu_4-grid complex (**3**).

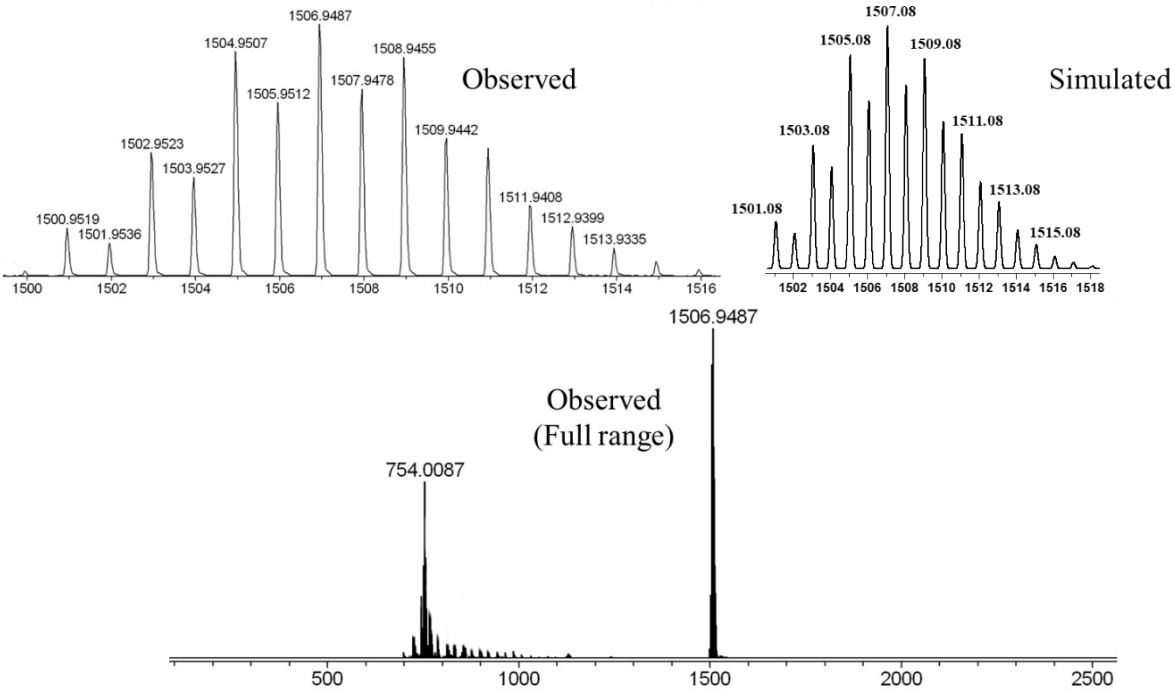

Fig. S6 Observed and simulated ESI-Mass spectra of Zn_4-grid complex (**4**).

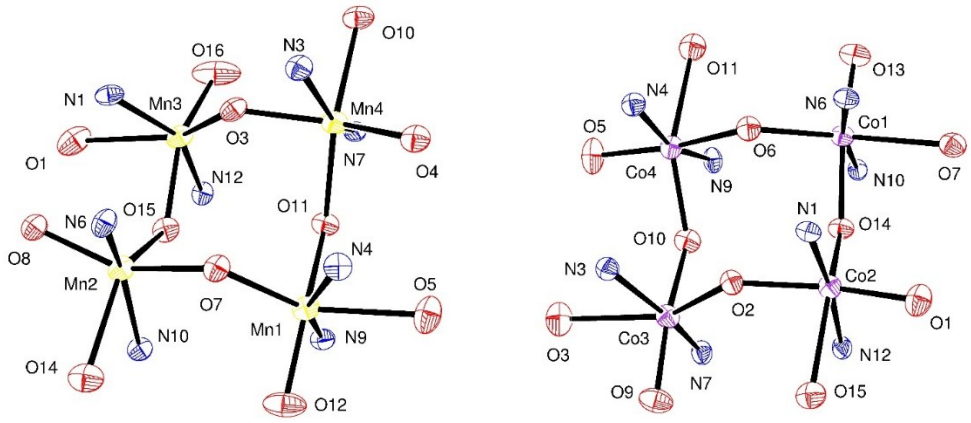

Fig. S7 The core structure of the complex **1** (left) and **2** (right).

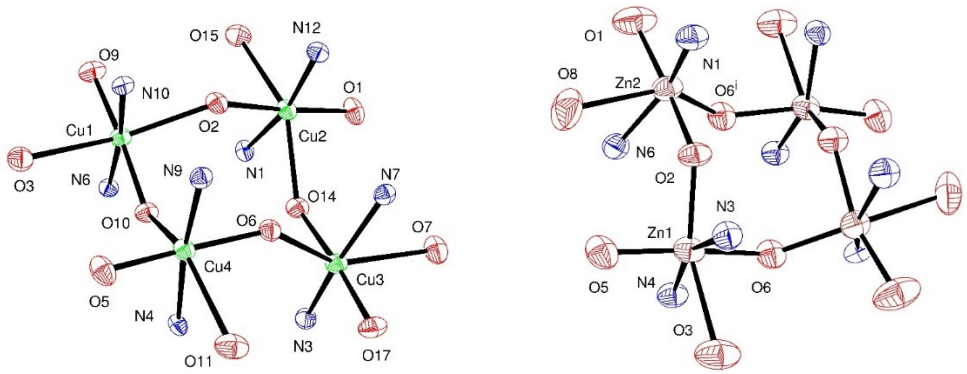

Fig. S8 The core structure of the complex **3** (left) and **4** (right).

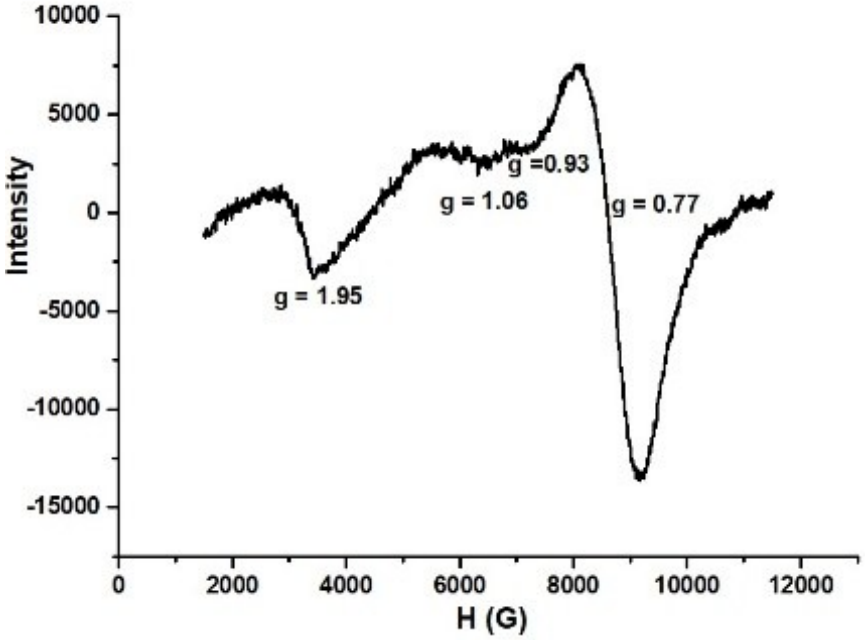

Fig. S9 X-band EPR spectra of **2** in solid state at room temperature (290 K).

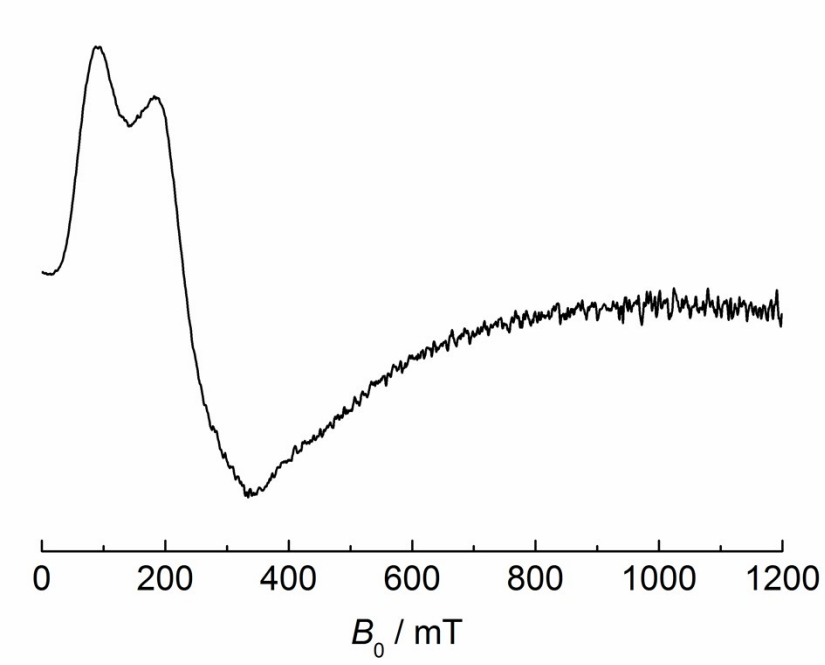

Fig. S10 Low-temperature (20 K) X-band EPR spectrum of a powder sample of compound 2 measured at a microwave frequency of 9.325225 GHz, indicating dominating zero-field splitting.

Table S1. Selected bond distances (Å) and angles (°) for complex **1**-**4**.

$[Mn_4L_4](CH_3CN)$ (1)		**$[Co_4L_4](CHCl_3)$ (2)**		**$[Cu_4L_4](CHCl_3)$ (3)**		**$[Zn_4L_4]$ (4)**	
Mn(1)-O(12)	2.0080(60)	Co(1)-O(16)	1.9420(20)	Cu(1)-O(9)	1.8891(19)	Zn(1)-O(5)	1.951(3)
Mn(1)-O(11)	2.1280(50)	Co(1)-N(12)	2.0270(20)	Cu(1)-N(6)	1.943(2)	Zn(1)-N(3)	2.111(3)
Mn(1)-O(7)	2.1370(50)	Co(1)-O(15)	2.0520(20)	Cu(1)-O(10)	1.9515(18)	Zn(1)-O(6)	2.093(3)
Mn(1)-N(9)	2.2070(70)	Co(1)-N(1)	2.0650(20)	Cu(1)-N(10)	2.044(2)	Zn(1)-N(4)	2.074(3)
Mn(1)-N(4)	2.2170(60)	Co(1)-O(3)	2.1070(20)	Cu(1)-O(2)	2.3102(19)	Zn(1)-O(2)	2.130(2)
Mn(1)-O(5)	2.4940(60)	Co(1)-O(2)	2.5190(20)	Cu(1)-O(3)	2.600(18)	Zn(1)-O(3)	2.578(2)
Mn(2)-O(8)	2.0270(50)	Co(2)-O(8)	1.9500(20)	Cu(2)-O(1)	1.882(2)	Zn(2)-O(1)	1.931(3)
Mn(2)-O(7)	2.1530(50)	Co(2)-N(6)	2.0530(20)	Cu(2)-N(12)	1.947(2)	Zn(2)-N(6)	2.099(3)
Mn(2)-N(6)	2.1960(50)	Co(2)-O(7)	2.0560(20)	Cu(2)-O(2)	1.9508(19)	Zn(2)-O(3)	2.101(2)
Mn(2)-O(15)	2.2230(50)	Co(2)-N(10)	2.0790(20)	Cu(2)-N(1)	2.069(2)	Zn(2)-N(1)	2.048(3)
Mn(2)-N(10)	2.2340(60)	Co(2)-O(15)	2.1110(20)	Cu(2)-O(14)	2.3203(19)	Zn(2)-O(8)	2.583(3)
Mn(2)-O(14)	2.4800(60)	Co(2)-O(14)	2.3800(20)	Cu(2)-O(15)	2.6440(18)	Zn(2)-O(7)#1	2.053(2)
		Co(3)-O(12)	1.9420(20)	Cu(3)-O(17)	1.896(2)		
Mn(3)-O(15)	2.1250(50)	Co(3)-N(9)	2.0370(30)	Cu(3)-N(3)	1.944(2)		
Mn(3)-O(3)	2.1630(50)	Co(3)-O(11)	2.0700(20)	Cu(3)-O(14)	1.9654(19)		
Mn(3)-N(12)	2.2130(70)	Co(3)-N(4)	2.0840(30)	Cu(3)-N(7)	2.064(2)		
Mn(3)-N(1)	2.2350(60)	Co(3)-O(7)	2.0980(20)	Cu(3)-O(6)	2.2904(19)		
Mn(3)-O(1)	2.5020(60)	Co(3)-O(6)	2.5420(20)	Cu(3)-O(7)	2.5930(18)		
Mn(4)-O(4)	2.0120(50)	Co(4)-O(4)	1.9350(20)	Cu(4)-O(5)	1.890(2)		

Mn(4)-O(3)	2.1440(50)	Co(4)-N(3)	2.0350(20)	Cu(4)-N(9)	1.955(2)		
Mn(4)-N(3)	2.2090(50)	Co(4)-O(3)	2.0470(20)	Cu(4)-O(6)	1.9590(19)		
Mn(4)-O(11)	2.2110(50)	Co(4)-N(7)	2.0960(30)	Cu(4)-N(4)	2.077(2)		
Mn(4)-N(7)	2.2230(60)	Co(4)-O(11)	2.1160(20)	Cu(4)-O(10)	2.3099(18)		
Mn(4)-O(10)	2.5200(50)	Co(4)-O(10)	2.6040(20)	Cu(4)-O(11)	2.596(2)		
Mn(1)-Mn(2)	3.8640(50)	Co(1)-Co(2)	3.8300(20)	Cu(1)-Cu(2)	4.004(2)	Zn(1)-Zn(2)	3.830(14)
Mn(2)-Mn(3)	3.9200(60)	Co(2)-Co(3)	3.8350(20)	Cu(2)-Cu(3)	4.0330(18)		
Mn(3)-Mn(4)	3.8850(60)	Co(3)-Co(4)	3.8720(30)	Cu(3)-Cu(4)	3.9860(20)		
Mn(4)-Mn(1)	3.9140(70)	Co(4)-Co(1)	3.8400(20)	Cu(4)-Cu(1)	3.9750(19)		
Mn(1)-O(7)-Mn(2)	128.50(20)	Co(1)-O(15)-Co(2)	133.90(10)	Cu(2)-O(2)-Cu(1)	139.85(9)	Zn(2)-O(3)-Zn(1)	134.95(7)
Mn(1)-O(11)-Mn(4)	128.90(20)	Co(2)-O(7)-Co(3)	134.84(10)	Cu(3)-O(14)-Cu(2)	140.30(9)		
Mn(3)-O(15)-Mn(2)	128.70(20)	Co(3)-O(11)-Co(4)	135.43(10)	Cu(4)-O(6)-Cu(3)	139.36(9)		
Mn(4)-O(3)-Mn(3)	128.90(20)	Co(4)-O(3)-Co(1)	135.20(10)	Cu(1)-O(10)-Cu(4)	137.58(9)		