Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Trinuclear heterometallic Cu^{II}–Mn^{II} complexes of a salen type Schiff base ligand: anion dependent variation of phenoxido bridging angles and magnetic coupling

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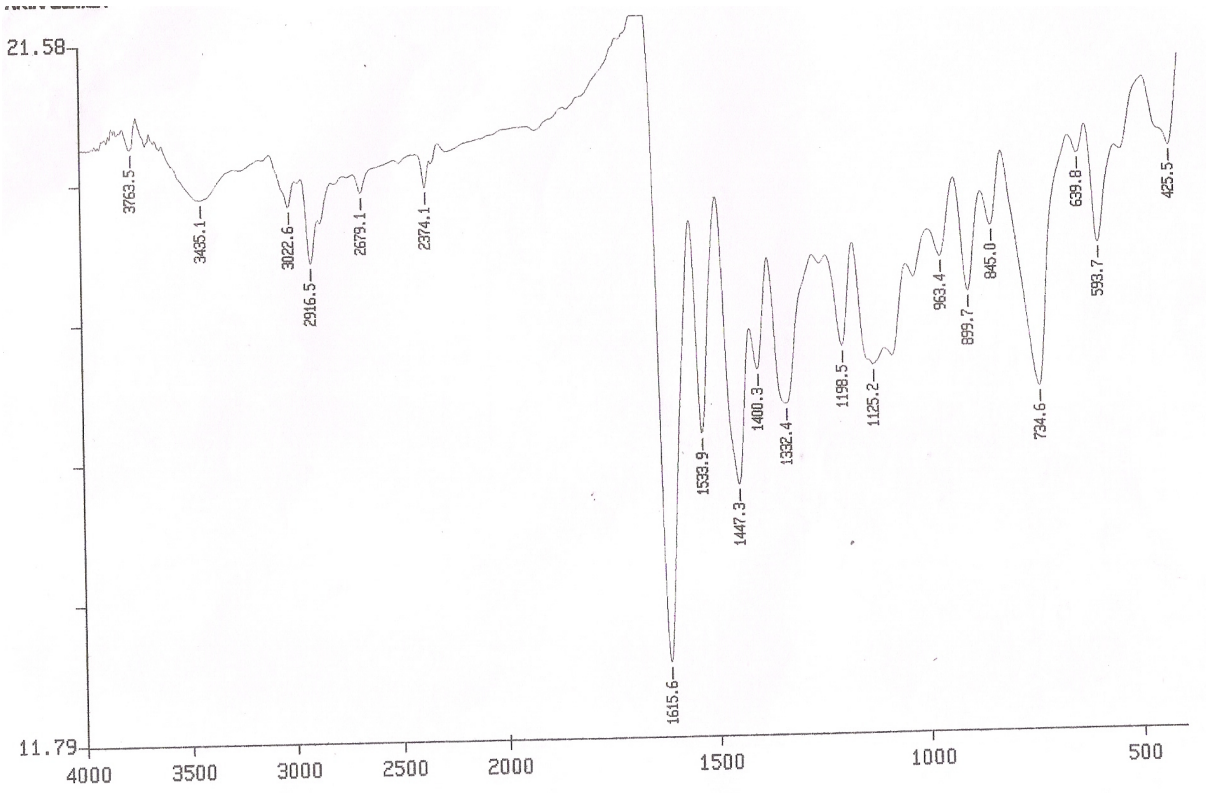

Figure S1: IR spectra of the metalloligand [CuL].

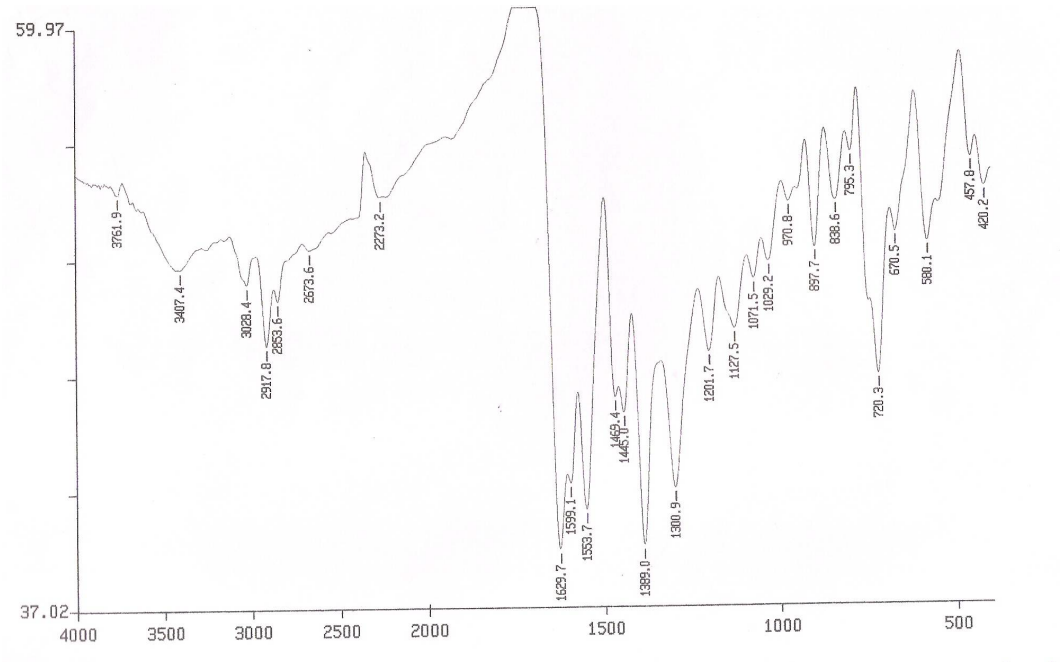

Figure S2: IR spectra of complex **1**.

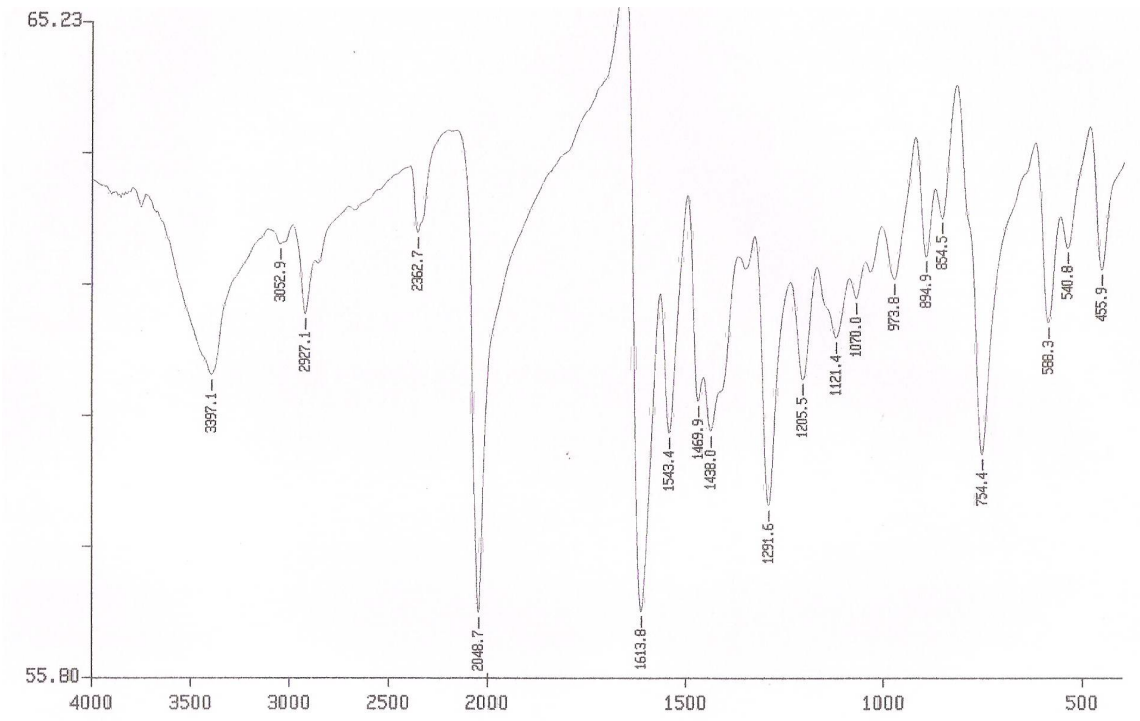

Figure S3: IR spectra of complex **2**.

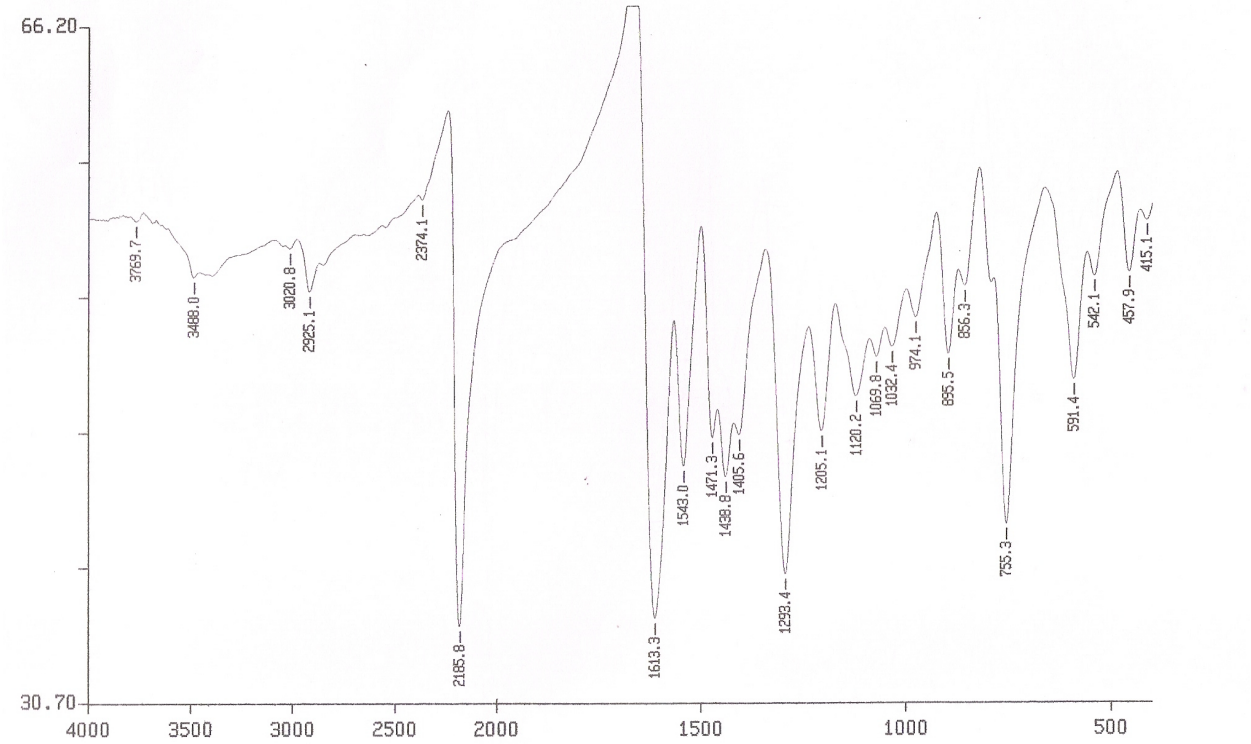

Figure S4: IR spectra of complex **3**.

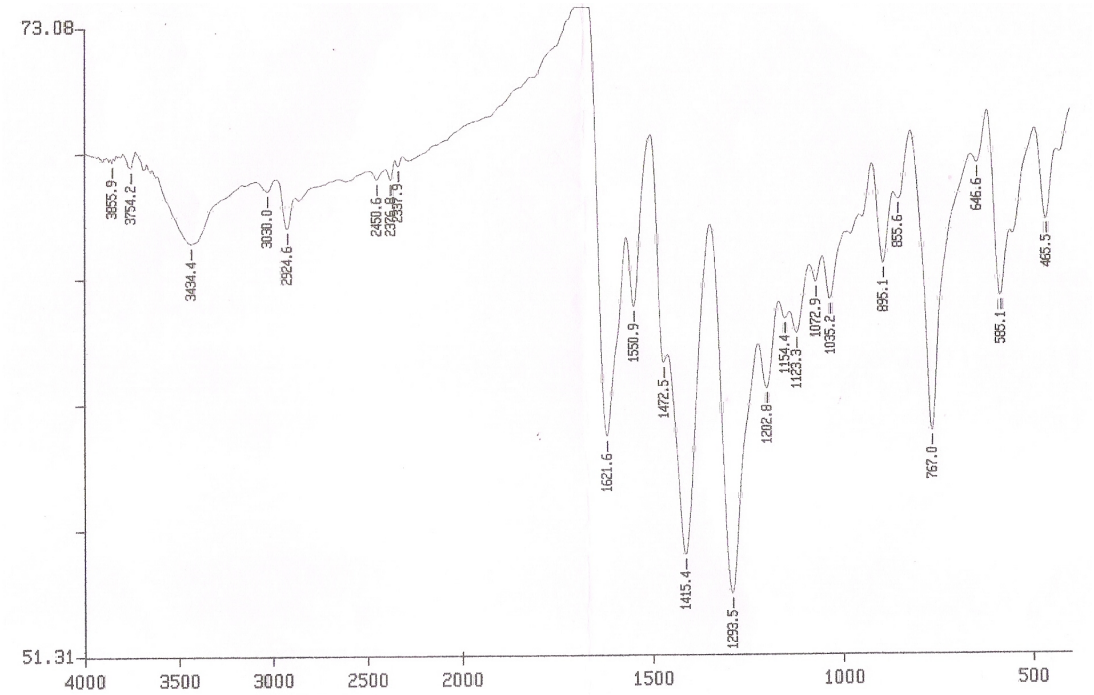

Figure S5: IR spectra of complex **4**.

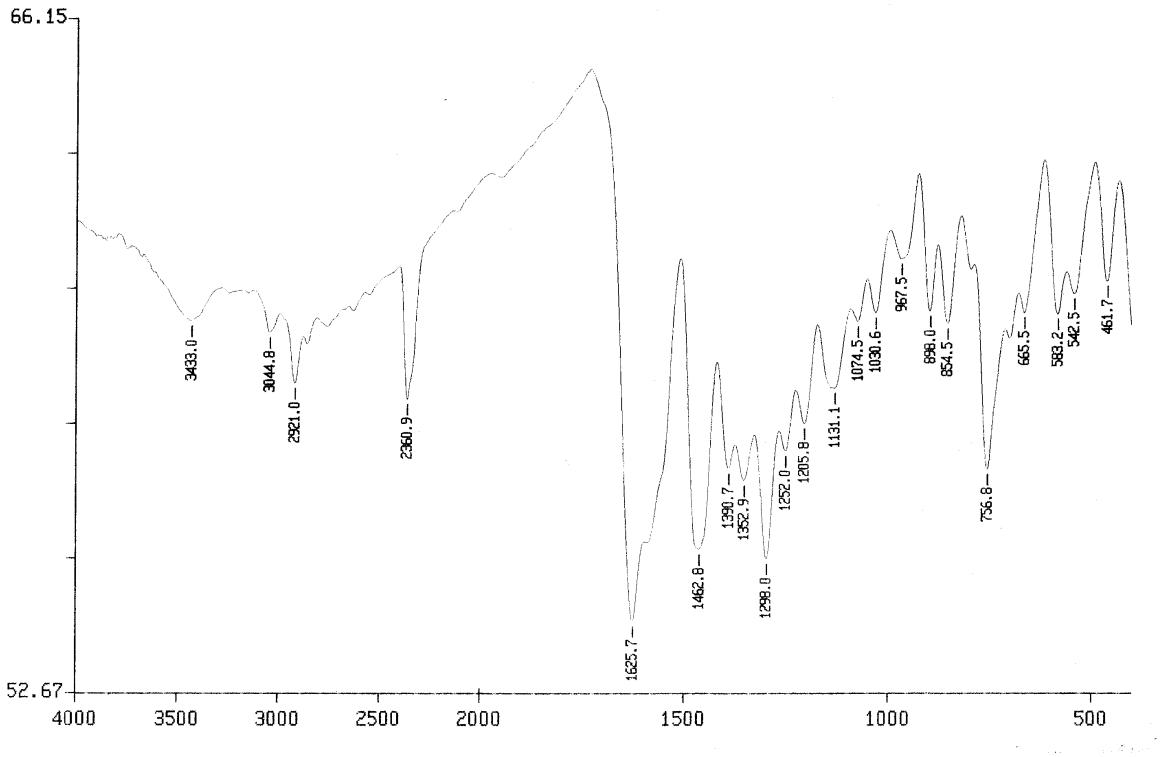

Figure S6: IR spectra of complex **5**.

Hydrogen bonding in Complexes **2-5**:

In Complex **2** the hydrogen atom H(8) from salicylaldehyde moiety forms a donor intermolecular hydrogen bond with azido nitrogen N(3) (1-x,-y,1-z) with dimensions C(11)···N(3) 3.43(3) Å, C(11)–H(8)···N(3) 163.1(2)º and H(8)···N(3) 2.47 Å to result in a 1D chain along the crystallographic *a* axis. (Fig. S7)

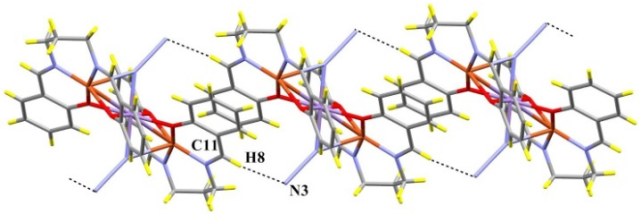

Figure S7: Hydrogen bonding in complex **2**.

Each of the isocyanato oxygen of complex **3** (O5, O6) participates in intermolecular hydrogen bonding with the hydrogen atoms (H7, H36, H15B) of ligand moiety with dimensions in the

range C···O 3.333(8)–3.393(6) Å, C–H···O 142.0(3)- 155.0(3)º and H···O 2.52-2.55 Å. (Fig. S8)

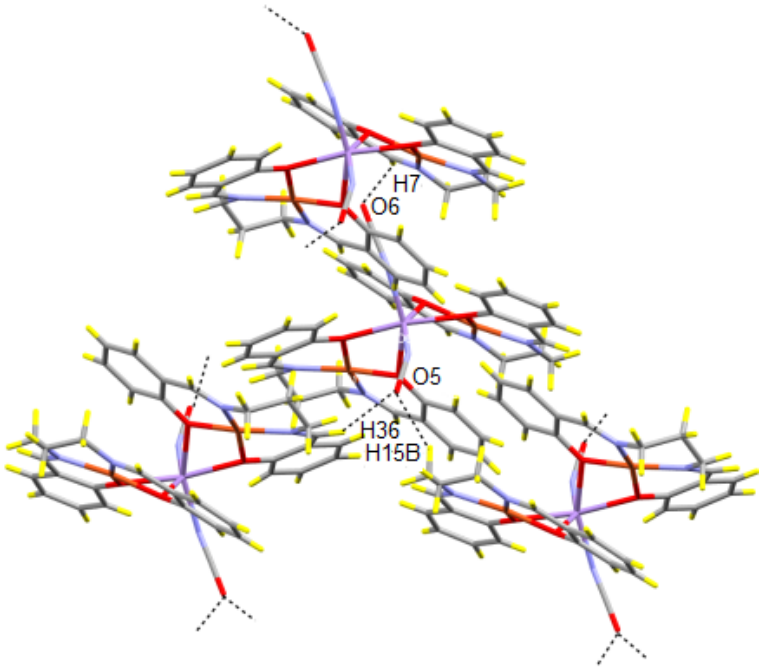

Figure S8. Hydrogen bonded polymeric structure in **3**.

In complex **4** the nitrato oxygen (O5) forms intermolecular hydrogen bonding with hydrogen atom (H10) of the ligand moiety with dimensions C(14)···O(5) 3.462(7) Å, C(14)–H(10)···O(5) 170(4)º and H(10)···O(5) 2.54 Å. (Fig. S9) In **5** phenolic oxygen (O5) of salicylate forms intermolecular hydrogen bonding with methylene hydrogen (H1B2) of dichloromethane solvent with dimensions C(1B)···O(5) 3.45(3) Å, C(1B)–H(1B2)···O(5) 148º and H(1B2)···O(5) 2.58 Å. (Fig. S10)

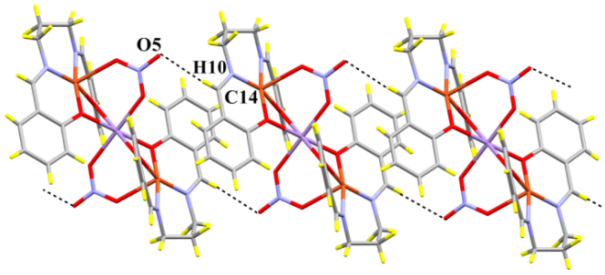

Figure S9. Hydrogen bonded 1D chain in **4**.

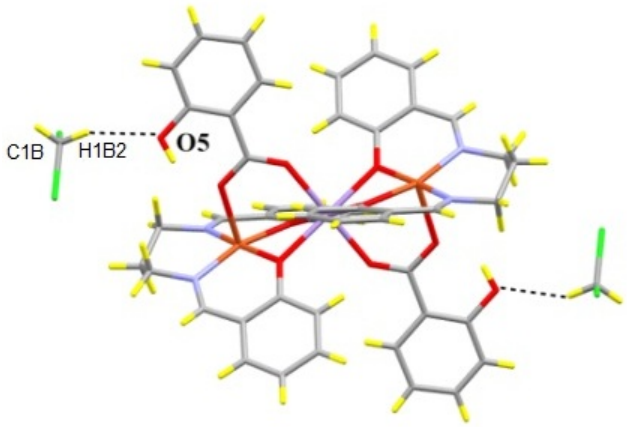

Figure S10. Hydrogen bonding with solvent molecule (CH_2Cl_2) in **5**.

ST 1 Bond distances (Å) and angles (º) in the metal coordination spheres of complex **1.**

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu(1)–O(1)	1.970(2)	Cu(2)–N(3)	1.981(4)
Cu(1)–O(2)	1.961(2)	Cu(2)–N(4)	1.997(3)
Cu(1)–O(5)	2.171(3)	Mn(3)–O(1)	2.198(2)
Cu(1)–N(1)	1.995(3)	Mn(3)–O(2)	2.176(2)
Cu(1)–N(2)	1.985(3)	Mn(3)–O(3)	2.172(2)
Cu(2)–O(3)	1.964(2)	Mn(3)–O(4)	2.214(2)
Cu(2)–O(4)	1.956(2)	Mn(3)–O(6)	2.159(2)
Cu(2)–O(8)	2.195(3)	Mn(3)–O(7)	2.172(2)
Atoms	Angle (º)	Atoms	Angle (º)
O(1)–Cu(1)–O(2)	81.85(9)	O(8)–Cu(2)–N(4)	92.76(1)
O(1)–Cu(1)–O(5)	95.75(9)	N(3)–Cu(2)–N(4)	95.52(1)
O(1)–Cu(1)–N(1)	90.19(1)	O(1)–Mn(3)–O(2)	72.13(8)
O(1)–Cu(1)–N(2)	167.27(1)	O(1)–Mn(3)–O(3)	108.12(8)
O(2)–Cu(1)–O(5)	96.69(9)	O(1)–Mn(3)–O(4)	176.70(8)
O(2)–Cu(1)–N(1)	166.94(1)	O(1)–Mn(3)–O(6)	89.04(9)
O(2)–Cu(1)–N(2)	91.27(1)	O(1)–Mn(3)–O(7)	91.41(9)
O(5)–Cu(1)–N(1)	94.39(1)	O(2)–Mn(3)–O(3)	178.78(9)
O(5)–Cu(1)–N(2)	95.68(1)	O(2)–Mn(3)–O(4)	108.17(8)

N(1)–Cu(1)–N(2)	94.50(1)	O(2)–Mn(3)–O(6)	87.10(8)
O(3)–Cu(2)–O(4)	81.85(9)	O(2)–Mn(3)–O(7)	93.20(8)
O(3)–Cu(2)–O(8)	96.24(1)	O(3)–Mn(3)–O(4)	71.65(8)
O(3)–Cu(2)–N(3)	90.34(1)	O(3)–Mn(3)–O(6)	94.10(8)
O(3)–Cu(2)–N(4)	168.73(1)	O(3)–Mn(3)–O(7)	85.60(8)
O(4)–Cu(2)–O(8)	94.70(9)	O(4)–Mn(3)–O(6)	87.70(8)
O(4)–Cu(2)–N(3)	167.62(1)	O(4)–Mn(3)–O(7)	91.86(8)
O(4)–Cu(2)–N(4)	90.68(1)	O(6)–Mn(3)–O(7)	179.52(9)
O(8)–Cu(2)–N(3)	95.69(12)	Cu(1)–O(1)–Mn(3)	97.71(9)

ST 2 Bond distances (Å) and angles (º) in the metal coordination spheres of complex **2.**

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu(1)–O(1)	1.9474(2)	Mn(3)–O(1)	2.2003(2)
Cu(1)–O(2)	1.9346(2)	Mn(3)–O(2)	2.1718(2)
Cu(1)–N(4)	1.9434(2)	Mn(3)–N(1)	2.194(2)
Cu(1)–N(5)	1.9726(2)	Mn(3)–O(1)^{a}	2.2003(2)
Cu(1)–N(1)^{a}	2.649(2)	Mn(3)–O(2)^{a}	2.1718(2)
		Mn(3)–N(1)^{a}	2.194(2)
Atoms	Angle (º)	Atoms	Angle (º)
O(1)–Cu(1)–O(2)	81.92(5)	O(1)–Mn(3)–O(2)^{a}	108.81(4)
O(1)–Cu(1)–N(4)	92.28(5)	O(1)–Mn(3)–N(1)^{a}	83.37(5)
O(1)–Cu(1)–N(5)	160.12(5)	O(2)–Mn(3)–N(1)	98.52(5)
O(1)–Cu(1)–N(1)^{a}	77.29(5)	O(1)^{a}–Mn(3)–O(2)	108.81(4)
O(2)–Cu(1)–N(4)	165.64(5)	O(2)–Mn(3)–O(2)^{a}	180.00
O(2)–Cu(1)–N(5)	91.47(5)	O(2)–Mn(3)–N(1)^{a}	81.48(5)
O(2)–Cu(1)–N(1)^{a}	75.06(5)	O(1)^{a}–Mn(3)–N(1)	83.37(5)
N(4)–Cu(1)–N(5)	98.09(6)	O(2)^{a}–Mn(3)–N(1)	81.48(5)
N(1)^{a}–Cu(1)–N(4)	90.89(6)	N(1)–Mn(3)–N(1)^{a}	180.00
N(1)^{a}–Cu(1)–N(5)	119.23(6)	O(1)^{a}–Mn(3)–O(2)^{a}	71.19(4)

O(1)–Mn(3)–O(2)	71.19(4)	O(1)[a]–Mn(3)–N(1)[a]	96.63(5)
O(1)–Mn(3)–N(1)	96.63(5)	O(2)[a]–Mn(3)–N(1)[a]	98.52(5)
O(1)–Mn(3)–O(1)[a]	180.00	Cu(1)–O(1)–Mn(3)	91.38(4)
		Cu(1)–O(2)–Mn(3)	92.60(4)

[a]= -x,-y,1-z

ST 3 Bond distances (Å) and angles (º) in the metal coordination spheres of complex **3.**

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu(1)–O(3)	1.937(3)	Cu(2)–N(2)	1.956(4)
Cu(1)–O(4)	1.922(3)	Mn(1)–O(1)	2.268(3)
Cu(1)–N(3)	1.957(4)	Mn(1)–O(2)	2.274(3)
Cu(1)–N(4)	1.982(4)	Mn(1)–O(3)	2.345(3)
Cu(2)–O(1)	1.924(3)	Mn(1)–O(4)	2.228(3)
Cu(2)–O(2)	1.916(3)	Mn(1)–N(5)	2.093(4)
Cu(2)–N(1)	1.960(4)	Mn(1)–N(6)	2.107(4)
Atoms	Angle (º)	Atoms	Angle (º)
O(3)–Cu(1)–O(4)	78.58(1)	O(1)–Mn(1)–O(2)	66.67(1)
O(3)–Cu(1)–N(3)	92.54(2)	O(1)–Mn(1)–O(3)	100.35(1)
O(3)–Cu(1)–N(4)	169.25(1)	O(1)–Mn(1)–O(4)	160.55(1)
O(4)–Cu(1)–N(3)	169.20(2)	O(1)–Mn(1)–N(5)	97.20(1)
O(4)–Cu(1)–N(4)	92.07(1)	O(1)–Mn(1)–N(6)	92.05(1)
N(3)–Cu(1)–N(4)	97.29(2)	O(2)–Mn(1)–O(3)	75.42(1)
O(1)–Cu(2)–O(2)	81.07(1)	O(2)–Mn(1)–O(4)	96.49(1)
O(1)–Cu(2)–N(1)	91.56(1)	O(2)–Mn(1)–N(5)	94.19(2)
O(1)–Cu(2)–N(2)	167.13(1)	O(2)–Mn(1)–N(6)	153.80(1)
O(2)–Cu(2)–N(1)	166.64(2)	O(3)–Mn(1)–O(4)	64.56(1)
O(2)–Cu(2)–N(2)	91.50(2)	O(3)–Mn(1)–N(5)	153.85(1)
N(1)–Cu(2)–N(2)	96.78(2)	O(3)–Mn(1)–N(6)	94.74(1)

		O(4)–Mn(1)–N(5)	93.57(1)
		O(4)–Mn(1)–N(6)	101.06(1)
		N(5)–Mn(1)–N(6)	103.89(2)
		Cu(2)–O(1)–Mn(1)	101.81(1)
		Cu(2)–O(2)–Mn(1)	101.89(1)
		Cu(1)–O(3)–Mn(1)	98.64(1)
		Cu(1)–O(4)–Mn(1)	103.22(1)

ST 4 Bond distances (Å) and angles (º) in the metal coordination spheres of complexes **4** and **5.**

	4	**5**
Cu(1)–O(1)	1.943(3)	1.963(3)
Cu(1)–O(2)	1.948(3)	1.957(4)
Cu(1)–O(3)	2.410(4)	2.248(5)
Cu(1)–N(1)	1.955(5)	1.995(5)
Cu(1)–N(2)	1.964(4)	1.973(5)
Mn(1)–O(1)	2.140(3)	2.159(4)
Mn(1)–O(2)	2.137(3)	2.194(3)
Mn(1)–O(4)	2.239(4)	2.151(4)
O(1) –Cu(1)–O(2)	82.49(1)	81.99(2)
O(1) –Cu(1)–O(3)	93.16(1)	98.37(2)
O(1) –Cu(1)–N(1)	90.72(2)	90.22(2)
O(1) –Cu(1)–N(2)	162.71(1)	165.90(2)
O(2) –Cu(1)–O(3)	91.10(1)	92.57(2)
O(2) –Cu(1)–N(1)	170.42(1)	171.31(2)
O(2) –Cu(1)–N(2)	91.26(1)	90.51(2)

O(3) –Cu(1)–N(1)	82.50(1)	92.38(2)
O(3) –Cu(1)–N(2)	103.09(1)	93.89(2)
N(1) –Cu(1)–N(2)	97.16(2)	96.30(2)
O(1)–Mn(1)–O(2)	73.72(1)	72.42(1)
O(1)–Mn(1)–O(4)	85.86(1)	89.01(2)
O(1)–Mn(1)–O(1)[a]	180.00	180.00
O(1)–Mn(1)–O(2)[a]	106.28(1)	107.58(1)
O(1)–Mn(1)–O(4)[a]	94.14(1)	91.00(1)
O(2)–Mn(1)–O(4)	88.68(13)	90.06(2)
O(2)–Mn(1)–O(2)[a]	180.00	180.00
O(2)–Mn(1)–O(4)[a]	91.33(1)	89.94(2)
O(4)–Mn(1)–O(4)[a]	180.00	180.00
Cu(1)–O(1)–Mn(1)	97.63(1)	98.20(1)
Cu(1)–O(2)–Mn(1)	97.54(1)	97.25(1)

[a]= 1-x,-y,-z in **4** and -x,-y,-z in **5**