

Electronic Supplementary Information

Syntheses and Structures of a Family of Heterometallic Pentanuclear $[\text{Mn}^{\text{III}}_3\text{LnNa}]$ (Ln = Dy, Tb, Gd and Nd) Complexes: H-bonding Reduces the Nuclearity From Nine to Five

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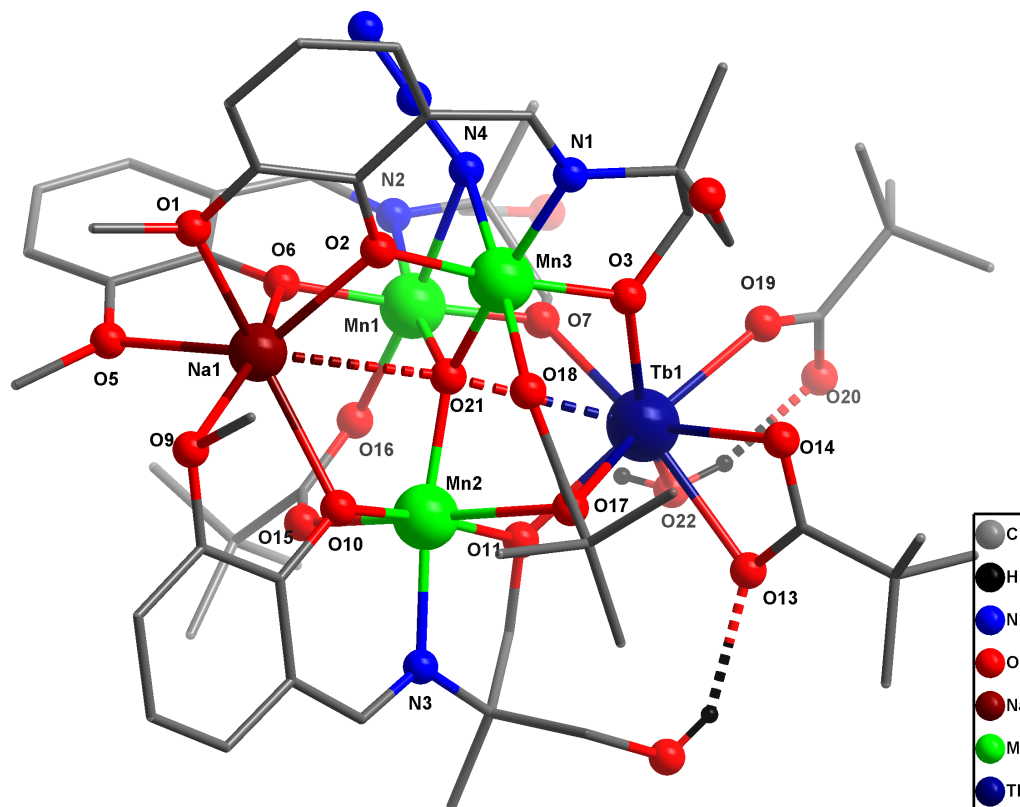


Figure S1. Molecular structure of **2**. All the hydrogen atoms (except those that take part in H-bonding) and a solvent molecule (water) have been omitted for clarity.

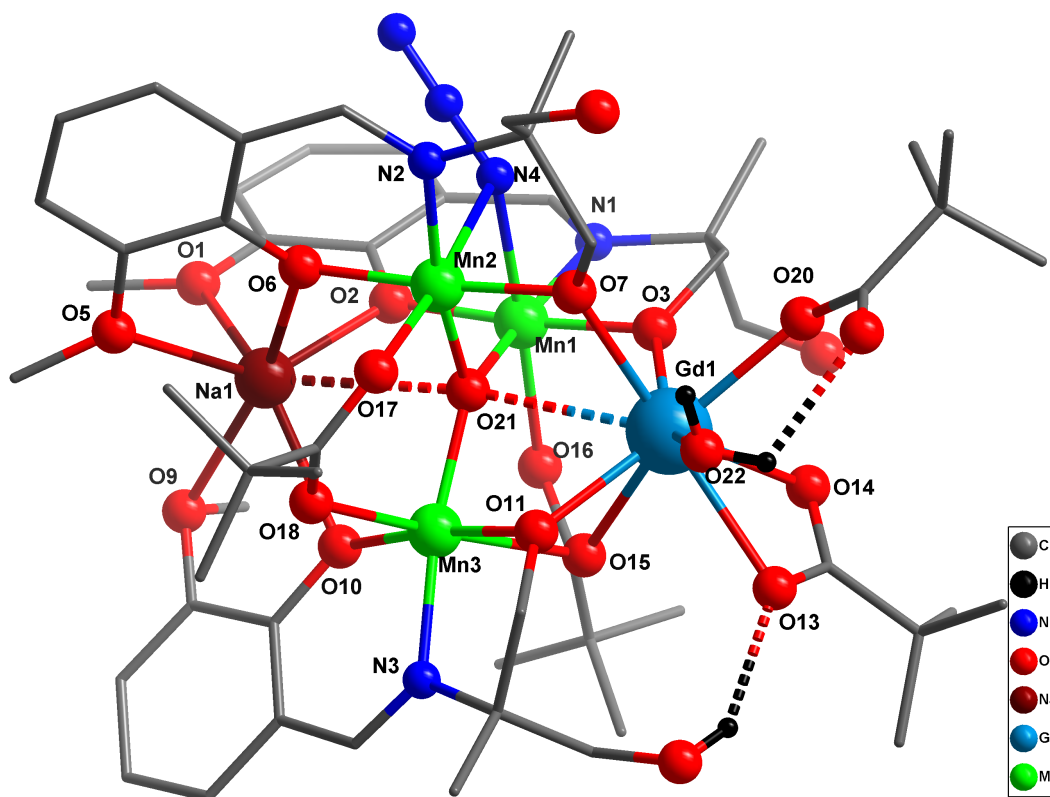


Figure S2. Molecular structure of **3**. All the hydrogen atoms (except those that take part in H-bonding) and a solvent molecule (water) have been omitted for clarity.

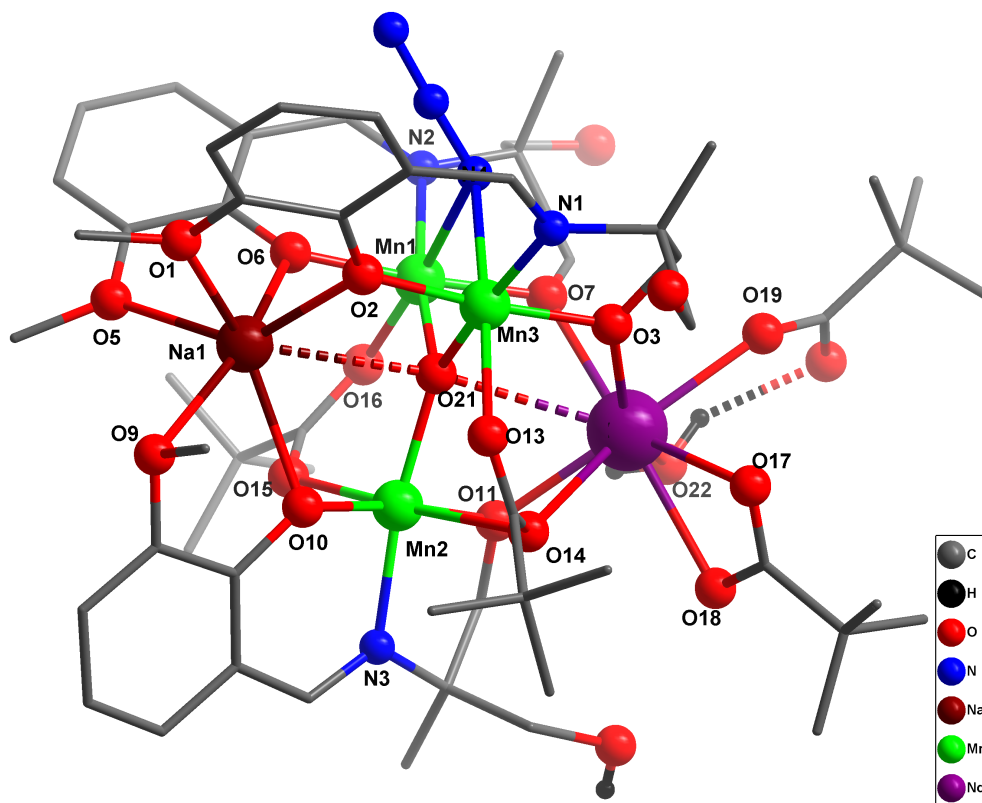


Figure S3. Molecular structure of **4**. All the hydrogen atoms (except those that take part in H-bonding) and a solvent molecule (water) have been omitted for clarity.

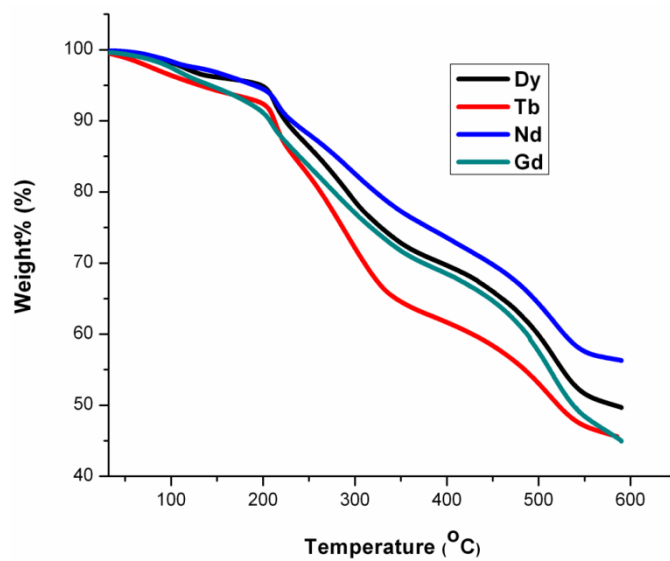


Figure S4. TGA of **1-4**.

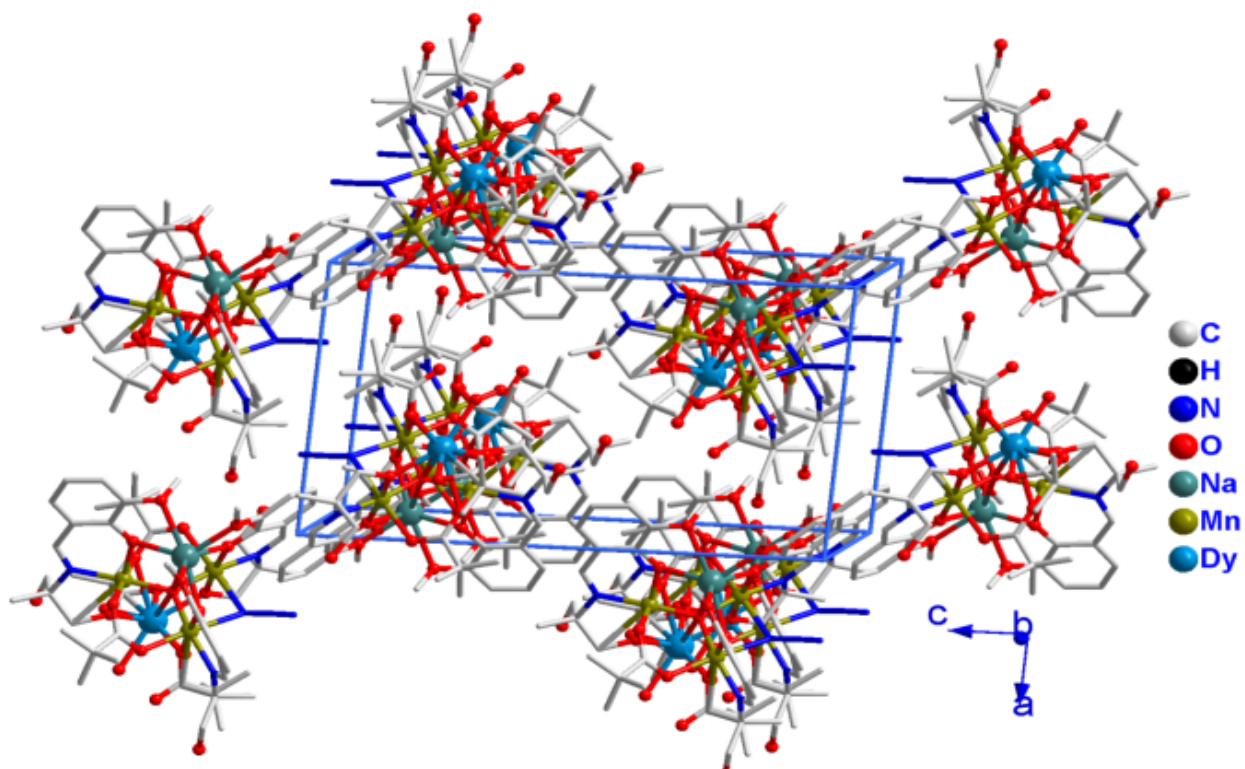


Figure S5. Packing diagram of **1** along the crystallographic 'b' axis.

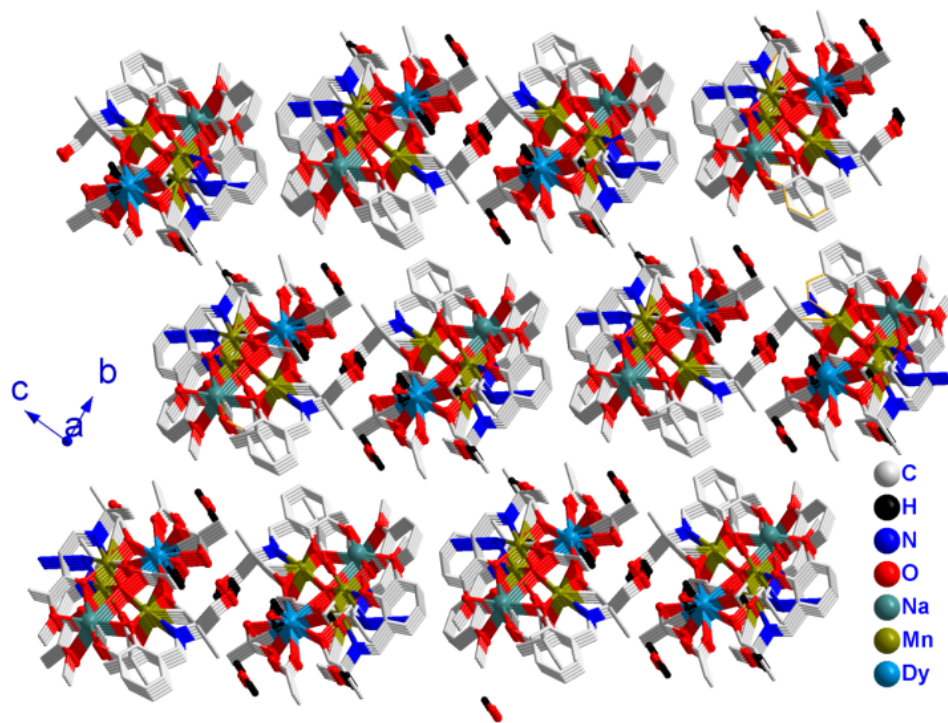


Figure S6. A 3-dimensional view of the one dimensional chain along the crystallographic 'a' axis of **1**.

Table S1. Comparison of the selected bond distances (Å) for **1–4**.

	Ln= Dy(1)	Ln= Tb (2)	Ln= Gd(3)	Ln= Nd(4)
Mn–O _{phenolate}	1.914(6)	1.908(4)	1.907(9)	1.898(6)
	1.886(6)	1.891(4)	1.901(9)	1.882(6)
	1.906(6)	1.897(4)	1.889(9)	1.892(6)
Mn–O _{alcoholic}	1.898(6)	1.882(4)	1.872(8)	1.870(6)
	1.875(5)	1.882(4)	1.896(8)	1.871(6)
	1.886(5)	1.881(4)	1.878(8)	1.874(6)
Mn–N _{imino}	2.001(7)	1.993(5)	2.014(11)	1.995(8)
	2.019(6)	2.027(5)	1.994(10)	2.024(7)
	2.020(7)	2.017(5)	2.011(10)	2.013(8)
Mn–N _{azide}	2.318(6)	2.334(5)	2.254(10)	2.337(8)
	2.235(6)	2.256(5)	2.340(10)	2.256(7)
Mn– μ_3 -O ²⁻	1.919(5)	1.911(4)	1.973(8)	1.919(6)
	1.929(5)	1.927(4)	1.907(8)	1.941(5)
	1.946(5)	1.957(4)	1.931(8)	1.974(6)
Mn– μ -OAc	2.164(5)	2.151(4)	2.166(8)	2.163(7)
	2.139(6)	2.143(5)	2.133(9)	2.144(7)
Mn– μ_3 -OAc	2.344(6)	2.350(4)	2.194(9)	2.200(7)
	2.192(5)	2.195(4)	2.357(9)	2.355(7)
Ln–O _{alcoholic}	2.363(6)	2.298(4)	2.311(8)	2.348(6)
	2.281(5)	2.379(4)	2.393(8)	2.457(6)
	2.274(5)	2.291(4)	2.309(8)	2.356(6)
Ln–OAc _{terminal}	2.313(6)	2.326(5)	2.320(10)	2.368(7)
Ln– η^2 -OAc	2.430(6)	2.455(5)	2.467(9)	2.513(7)
	2.454(6)	2.445(5)	2.470(9)	2.516(6)
Ln–OH _{2terminal}	2.413(6)	2.407(5)	2.444(9)	2.498(7)
Ln– μ_3 -OAc	2.726(6)	2.750(4)	2.691(9)	2.752(7)
Ln----- μ_3 -O ²⁻	2.857(5)	2.882(4)	2.838(8)	2.881(6)
Na–O _{OMe}	2.435(7)			
	2.545(7)	2.428(6)	2.404(10)	2.425(8)
	2.425(7)	2.420(6)	2.437(10)	2.422(9)
		2.550(5)	2.543(11)	2.551(8)
Na–O _{phenolate}	2.322(7)			
	2.407(6)	2.341(5)	2.328(10)	2.337(8)
	2.337(7)	2.321(5)	2.341(10)	2.319(8)
		2.412(5)	2.405(10)	2.406(7)
Na----- μ_3 -O ²⁻	2.844(6)	2.843(5)	2.873(9)	2.854(7)

Mn-----Mn	3.312(2)	3.313(2)	3.115(3)	3.329(2)
	3.109(2)	3.112(2)	3.590(3)	3.129(2)
	3.568(2)	3.569(2)	3.312(3)	3.601(2)
Mn-----Ln	3.560(2)	3.575(1)	3.526(2)	3.61 (2)
	3.347(2)	3.360(1)	3.571(2)	3.385(2)
	3.514(1)	3.531(1)	3.351(2)	3.561(2)
Mn-----Na	3.493(4)	3.496(3)	3.359(5)	3.491(4)
	3.354(4)	3.358(3)	3.441(6)	3.352(4)
	3.436(4)	3.444(3)	3.501(5)	3.436(4)
Na-----Ln	5.689(3)	5.712(1)	5.697(5)	5.721(4)

Table S2. Selected bond distances (Å) and bond angles (°) for compound **1(Mn₃DyNa)**.

Bond Lengths around Manganese(1)	Bond Angles around Manganese(1)	O(3)-Dy(1)-O(14) 148.0(2)
N(1)-Mn(1) 2.001(7)	O(3)-Mn(1)-O(2) 176.3(2)	O(22)-Dy(1)-O(14) 115.8(2)
N(4)-Mn(1) 2.318(6)	O(3)-Mn(1)-O(21) 90.5(2)	O(13)-Dy(1)-O(14) 52.5(2)
O(2)-Mn(1) 1.914(6)	O(2)-Mn(1)-O(21) 92.9(2)	O(11)-Dy(1)-O(17) 74.93(18)
O(3)-Mn(1) 1.898(6)	O(3)-Mn(1)-N(1) 84.3(3)	O(7)-Dy(1)-O(17) 65.28(18)
O(15)-Mn(1) 2.164(5)	O(2)-Mn(1)-N(1) 92.1(3)	O(19)-Dy(1)-O(17) 145.8(2)
O(21)-Mn(1) 1.919(5)	O(21)-Mn(1)-N(1) 169.6(3)	O(3)-Dy(1)-O(17) 120.95(17)
Bond Lengths around Manganese(2)	O(3)-Mn(1)-O(15) 92.2(2)	O(22)-Dy(1)-O(17) 133.03(19)
N(2)-Mn(2) 2.019(6)	O(2)-Mn(1)-O(15) 88.4(2)	O(13)-Dy(1)-O(17) 76.84(19)
O(6)-Mn(2) 1.886(6)	O(21)-Mn(1)-O(15) 102.4(2)	O(14)-Dy(1)-O(17) 72.7(2)
O(7)-Mn(2) 1.875(5)	N(1)-Mn(1)-O(15) 86.9(2)	O(11)-Dy(1)-O(21) 62.34(17)
O(16)-Mn(2) 2.139(6)	O(3)-Mn(1)-N(4) 88.9(2)	O(7)-Dy(1)-O(21) 62.51(17)
O(17)-Mn(2) 2.344(6)	O(2)-Mn(1)-N(4) 90.2(2)	O(19)-Dy(1)-O(21) 129.99(18)
O(21)-Mn(2) 1.929(5)	O(21)-Mn(1)-N(4) 82.5(2)	O(3)-Dy(1)-O(21) 61.74(17)
Bond Lengths around Manganese(3)	N(1)-Mn(1)-N(4) 88.3(2)	O(22)-Dy(1)-O(21) 121.90(19)
N(3)-Mn(3) 2.020(7)	O(15)-Mn(1)-N(4) 174.9(2)	O(13)-Dy(1)-O(21) 132.81(18)
N(4)-Mn(3) 2.235(6)	Bond Angles around Manganese(2)	O(14)-Dy(1)-O(21) 120.78(19)
O(10)-Mn(3) 1.906(6)	O(7)-Mn(2)-O(6) 172.7(2)	O(17)-Dy(1)-O(21) 59.34(15)
O(11)-Mn(3) 1.886(5)	O(7)-Mn(2)-O(21) 90.9(2)	Bond Angles around Sodium
O(18)-Mn(3) 2.192(5)		O(2)-Na(1)-O(10) 92.4(2)
		O(2)-Na(1)-O(6) 116.2(2)

O(21)-Mn(3) 1.946(5)	O(6)-Mn(2)-O(21) 94.1(2)	O(10)-Na(1)-O(6) 98.0(2)
Bond Lengths around Dysprosium	O(7)-Mn(2)-N(2) 82.9(3)	O(2)-Na(1)-O(9) 109.8(2)
O(3)-Dy(1) 2.363(6)	O(6)-Mn(2)-N(2) 91.7(3)	O(10)-Na(1)-O(9) 65.9(2)
O(7)-Dy(1) 2.281(5)	O(21)-Mn(2)-N(2) 172.2(3)	O(6)-Na(1)-O(9) 131.9(2)
O(11)-Dy(1) 2.274(5)	O(7)-Mn(2)-O(16) 95.0(2)	O(2)-Na(1)-O(1) 65.7(2)
O(13)-Dy(1) 2.430(6)	O(6)-Mn(2)-O(16) 89.6(2)	O(10)-Na(1)-O(1) 139.8(3)
O(14)-Dy(1) 2.454(6)	O(21)-Mn(2)-O(16) 98.3(2)	O(6)-Na(1)-O(1) 121.6(3)
O(17)-Dy(1) 2.726(6)	N(2)-Mn(2)-O(16) 86.9(3)	O(9)-Na(1)-O(1) 89.4(3)
O(19)-Dy(1) 2.313(6)	O(7)-Mn(2)-O(17) 79.7(2)	O(2)-Na(1)-O(5) 164.2(3)
O(21)-Dy(1) 2.857(5)	O(6)-Mn(2)-O(17) 96.0(2)	O(10)-Na(1)-O(5) 103.1(2)
O(22)-Dy(1) 2.413(6)	O(21)-Mn(2)-O(17) 80.0(2)	O(6)-Na(1)-O(5) 65.3(2)
Bond Lengths around Sodium	N(2)-Mn(2)-O(17) 94.2(2)	O(9)-Na(1)-O(5) 74.5(2)
O(1)-Na(1) 2.435(7)	O(16)-Mn(2)-O(17) 174.3(2)	O(1)-Na(1)-O(5) 99.7(2)
O(2)-Na(1) 2.322(7)	Bond Angles around Manganese(3)	O(2)-Na(1)-O(21) 64.10(19)
O(5)-Na(1) 2.545(7)	O(11)-Mn(3)-O(10) 173.8(2)	O(10)-Na(1)-O(21) 66.38(19)
O(6)-Na(1) 2.407(6)	O(11)-Mn(3)-O(21) 89.7(2)	O(6)-Na(1)-O(21) 63.63(18)
O(9)-Na(1) 2.425(7)	O(10)-Mn(3)-O(21) 96.2(2)	O(9)-Na(1)-O(21) 131.5(2)
O(10)-Na(1) 2.337(7)	O(11)-Mn(3)-N(3) 82.3(3)	O(1)-Na(1)-O(21) 123.3(2)
O(21)-Na(1) 2.844(6)	O(10)-Mn(3)-N(3) 91.7(3)	O(5)-Na(1)-O(21) 125.1(2)
Bond Lengths containing Sodium and Manganese	O(21)-Mn(3)-N(3) 170.7(3)	Bond Angles containing Manganese and Dysprosium
Na(1)-Mn(1) 3.493(4)	O(11)-Mn(3)-O(18) 92.6(2)	Mn(1)-O(3)-Dy(1) 112.8(2)
Na(1)-Mn(2) 3.354(4)	O(10)-Mn(3)-O(18) 89.1(2)	Mn(2)-O(7)-Dy(1) 106.9(2)
Na(1)-Mn(3) 3.436(4)	O(21)-Mn(3)-O(18) 93.5(2)	Mn(3)-O(11)-Dy(1) 115.0(3)
Bond Lengths containing Manganese-Manganese	N(3)-Mn(3)-O(18) 91.4(3)	Mn(2)-O(17)-Dy(1) 82.26(18)
Mn(1)-Mn(2) 3.312(2)	O(11)-Mn(3)-N(4) 89.0(2)	Mn(1)-O(21)-Dy(1) 94.31(18)
Mn(1)-Mn(3) 3.109(2)	O(10)-Mn(3)-N(4) 89.6(2)	Mn(2)-O(21)-Dy(1) 86.45(17)
Mn(2)-Mn(3) 3.568(2)	O(21)-Mn(3)-N(4) 84.2(2)	Mn(3)-O(21)-Dy(1) 92.05(19)
Bond Lengths containing Manganese-Dysprosium	N(3)-Mn(3)-N(4) 91.1(3)	Bond Angles containing Manganese and Sodium
Mn(1)-Dy(1) 3.560(2)	O(18)-Mn(3)-N(4) 177.2(2)	Mn(1)-O(2)-Na(1) 110.8(3)
Mn(2)-Dy(1) 3.347(2)	Bond Angles around Dysprosium	Mn(2)-O(6)-Na(1) 102.1(2)
Mn(3)-Dy(1) 3.514(1)	O(11)-Dy(1)-O(7) 122.85(19)	Mn(3)-O(10)-Na(1) 107.7(3)
Bond Length containing Sodium-Dysprosium	O(11)-Dy(1)-O(19) 82.6(2)	Mn(1)-O(21)-Na(1) 92.3(2)
Na(1)-Dy(1) 5.689(3)	O(7)-Dy(1)-O(19) 148.3(2)	Mn(2)-O(21)-Na(1) 87.06(19)
	O(11)-Dy(1)-O(3) 81.94(19)	Mn(3)-O(21)-Na(1) 89.62(19)
	O(7)-Dy(1)-O(3) 85.06(19)	
	O(19)-Dy(1)-O(3) 80.0(2)	Bond Angles containing
	O(11)-Dy(1)-O(22) 151.4(2)	
	O(7)-Dy(1)-O(22) 75.1(2)	

	O(19)-Dy(1)-O(22)	74.5(2)	Manganese(1), Manganese(2) and Manganese(3)	
	O(3)-Dy(1)-O(22)	77.55(19)		
	O(11)-Dy(1)-O(13)	124.5(2)		
	O(7)-Dy(1)-O(13)	84.82(19)		
	O(19)-Dy(1)-O(13)	95.9(2)		Mn(3)-N(4)-Mn(1) 86.1(2)
	O(3)-Dy(1)-O(13)	152.7(2)		Mn(1)-O(21)-Mn(2) 118.8(3)
	O(22)-Dy(1)-O(13)	75.4(2)		Mn(1)-O(21)-Mn(3) 107.1(2)
	O(11)-Dy(1)-O(14)	73.8(2)		Mn(2)-O(21)-Mn(3) 134.0(3)
	O(7)-Dy(1)-O(14)	125.7(2)		
	O(19)-Dy(1)-O(14)	76.5(2)		

Table S3. Selected bond distances (Å) and bond angles (°) for compound **2(Mn₃TbNa)**.

Bond Lengths around Manganese(1)	Bond Angles around Manganese(1)	O(11)-Tb(1)-O(13) 84.13(15)
N(2)-Mn(1) 1.993(5)	O(7)-Mn(1)-O(6) 176.23(19)	O(3)-Tb(1)-O(13) 124.65(16)
N(4)-Mn(1) 2.334(5)	O(7)-Mn(1)-O(21) 90.72(18)	O(19)-Tb(1)-O(13) 97.01(17)
O(6)-Mn(1) 1.908(4)	O(6)-Mn(1)-O(21) 92.58(18)	O(7)-Tb(1)-O(13) 153.46(15)
O(7)-Mn(1) 1.882(4)	O(7)-Mn(1)-N(2) 84.4(2)	O(22)-Tb(1)-O(13) 75.23(16)
O(16)-Mn(1) 2.151(4)	O(6)-Mn(1)-N(2) 92.0(2)	O(14)-Tb(1)-O(13) 53.03(15)
O(21)-Mn(1) 1.911(4)	O(21)-Mn(1)-N(2) 170.2(2)	O(11)-Tb(1)-O(17) 65.16(14)
Bond Lengths around Manganese(2)	O(7)-Mn(1)-O(16) 92.93(18)	O(3)-Tb(1)-O(17) 74.48(14)
N(3)-Mn(2) 2.027(5)	O(6)-Mn(1)-O(16) 88.11(18)	O(19)-Tb(1)-O(17) 145.82(15)
O(10)-Mn(2) 1.891(4)	O(21)-Mn(1)-O(16) 102.56(17)	O(7)-Tb(1)-O(17) 120.01(13)
O(15)-Mn(2) 2.143(5)	N(2)-Mn(1)-O(16) 86.3(2)	O(22)-Tb(1)-O(17) 133.04(15)
O(17)-Mn(2) 2.350(4)	O(7)-Mn(1)-N(4) 88.96(19)	O(14)-Tb(1)-O(17) 72.88(15)
O(11)-Mn(2) 1.882(4)	O(6)-Mn(1)-N(4) 89.64(19)	O(13)-Tb(1)-O(17) 76.39(14)
O(21)-Mn(2) 1.927(4)	O(21)-Mn(1)-N(4) 83.20(18)	O(11)-Tb(1)-O(21) 62.30(13)
Bond Lengths around Manganese(3)	N(2)-Mn(1)-N(4) 88.1(2)	O(3)-Tb(1)-O(21) 62.18(13)
N(1)-Mn(3) 2.017(5)	O(16)-Mn(1)-N(4) 173.90(18)	O(19)-Tb(1)-O(21) 129.70(15)
N(4)-Mn(3) 2.256(5)	Bond Angles around Manganese(2)	O(7)-Tb(1)-O(21) 60.85(13)
O(2)-Mn(3) 1.897(4)	O(11)-Mn(2)-O(10) 172.31(19)	O(22)-Tb(1)-O(21) 122.08(14)
O(3)-Mn(3) 1.881(4)	O(11)-Mn(2)-O(21) 91.27(18)	O(14)-Tb(1)-O(21) 120.87(14)
O(18)-Mn(3) 2.195(4)	O(10)-Mn(2)-O(21) 94.04(18)	O(13)-Tb(1)-O(21) 132.07(14)
O(21)-Mn(3) 1.957(4)	O(11)-Mn(2)-N(3) 82.5(2)	O(17)-Tb(1)-O(21) 59.27(12)
Bond Lengths around Terbium	O(10)-Mn(2)-N(3) 91.8(2)	Bond Angles around Sodium
	O(21)-Mn(2)-N(3) 172.6(2)	O(6)-Na(1)-O(2) 91.71(18)
	O(11)-Mn(2)-O(15) 94.86(18)	O(6)-Na(1)-O(10) 116.27(18)
		O(2)-Na(1)-O(10) 97.59(18)
		O(6)-Na(1)-O(5) 66.31(17)
		O(2)-Na(1)-O(5) 139.9(2)

O(3)-Tb(1) 2.298(4)	O(10)-Mn(2)-O(15) 89.94(19)	O(10)-Na(1)-O(5) 122.0(2)
O(14)-Tb(1) 2.445(5)	O(21)-Mn(2)-O(15) 97.71(17)	O(6)-Na(1)-O(1) 109.79(19)
O(7)-Tb(1) 2.379(4)	N(3)-Mn(2)-O(15) 86.8(2)	O(2)-Na(1)-O(1) 66.00(18)
O(11)-Tb(1) 2.291(4)	O(11)-Mn(2)-O(17) 79.92(17)	O(10)-Na(1)-O(1) 131.51(19)
O(13)-Tb(1) 2.455(5)	O(10)-Mn(2)-O(17) 95.44(18)	O(5)-Na(1)-O(1) 89.44(19)
O(17)-Tb(1) 2.750(4)	O(21)-Mn(2)-O(17) 80.67(16)	O(6)-Na(1)-O(9) 164.1(2)
O(19)-Tb(1) 2.326(5)	N(3)-Mn(2)-O(17) 94.29(19)	O(2)-Na(1)-O(9) 103.92(19)
O(21)-Tb(1) 2.882(4)	O(15)-Mn(2)-O(17) 174.46(17)	O(10)-Na(1)-O(9) 64.97(17)
O(22)-Tb(1) 2.407(5)		O(5)-Na(1)-O(9) 99.15(19)
Bond Lengths around Sodium	Bond Angles around Manganese(3)	O(1)-Na(1)-O(9) 74.98(18)
O(1)-Na(1) 2.428(6)	O(3)-Mn(3)-O(2) 173.61(19)	O(6)-Na(1)-O(21) 63.70(14)
O(2)-Na(1) 2.341(5)	O(3)-Mn(3)-O(21) 90.28(18)	O(2)-Na(1)-O(21) 66.11(15)
O(5)-Na(1) 2.420(6)	O(2)-Mn(3)-O(21) 95.72(19)	O(10)-Na(1)-O(21) 63.60(14)
O(9)-Na(1) 2.550(5)	O(3)-Mn(3)-N(1) 82.1(2)	O(5)-Na(1)-O(21) 123.38(18)
O(10)-Na(1) 2.412(5)	O(2)-Mn(3)-N(1) 91.7(2)	O(1)-Na(1)-O(21) 131.33(18)
O(21)-Na(1) 2.843(5)	O(21)-Mn(3)-N(1) 170.9(2)	O(9)-Na(1)-O(21) 125.20(17)
O(6)-Na(1) 2.321(5)	O(3)-Mn(3)-O(18) 92.44(18)	Bond Angles containing Manganese and Terbium
Bond Lengths containing Sodium and Manganese	O(2)-Mn(3)-O(18) 89.34(18)	Mn(3)-O(3)-Tb(1) 114.9(2)
Na(1)-Mn(1) 3.496(3)	O(21)-Mn(3)-O(18) 93.78(16)	Mn(1)-O(7)-Tb(1) 113.58(19)
Na(1)-Mn(2) 3.358(3)	N(1)-Mn(3)-O(18) 91.53(19)	Mn(2)-O(11)-Tb(1) 106.82(18)
Na(1)-Mn(3) 3.444(3)	O(3)-Mn(3)-N(4) 89.5(2)	Mn(2)-O(17)-Tb(1) 82.00(13)
	O(2)-Mn(3)-N(4) 88.9(2)	Mn(1)-O(21)-Tb(1) 94.28(15)
	O(21)-Mn(3)-N(4) 84.29(18)	Mn(2)-O(21)-Tb(1) 86.23(14)
	N(1)-Mn(3)-N(4) 90.6(2)	Mn(3)-O(21)-Tb(1) 91.67(15)
	O(18)-Mn(3)-N(4) 177.28(18)	
Bond Lengths containing Manganese-Manganese	Bond Angles around Terbium	Bond Angles containing Manganese and Sodium
Mn(1)-Mn(2) 3.313(2)	O(11)-Tb(1)-O(3) 122.38(15)	Mn(3)-O(2)-Na(1) 108.3(2)
Mn(1)-Mn(3) 3.112(2)	O(11)-Tb(1)-O(19) 148.49(16)	Mn(1)-O(6)-Na(1) 111.1(2)
Mn(2)-Mn(3) 3.569(2)	O(3)-Tb(1)-O(19) 82.75(16)	Mn(2)-O(10)-Na(1) 101.93(19)
Bond Lengths containing Manganese-Terbium	O(11)-Tb(1)-O(7) 84.89(15)	Mn(1)-O(21)-Na(1) 92.57(16)
Mn(1)-Tb(1) 3.575(1)	O(3)-Tb(1)-O(7) 81.44(15)	Mn(2)-O(21)-Na(1) 87.28(15)
Mn(2)-Tb(1) 3.360(1)	O(19)-Tb(1)-O(7) 80.29(16)	Mn(3)-O(21)-Na(1) 89.75(16)
Mn(3)-Tb(1) 3.531(1)	O(11)-Tb(1)-O(22) 75.36(16)	Bond Angles containing Manganese(1), Manganese(2) and Manganese(3)
	O(3)-Tb(1)-O(22) 151.90(16)	Mn(1)-O(21)-Mn(2) 119.4(2)
Bond Length containing sodium-Terbium	O(19)-Tb(1)-O(22) 74.54(17)	Mn(1)-O(21)-Mn(3) 107.13(19)
Na(1)-Tb(1) 5.712(1)	O(7)-Tb(1)-O(22) 78.64(16)	Mn(2)-O(21)-Mn(3) 133.5(2)
	O(11)-Tb(1)-O(14) 125.82(16)	Mn(3)-N(4)-Mn(1) 85.35(18)
	O(3)-Tb(1)-O(14) 73.72(16)	
	O(19)-Tb(1)-O(14) 76.49(17)	
	O(7)-Tb(1)-O(14) 147.73(15)	
	O(22)-Tb(1)-O(14) 115.54(17)	

Table S4. Selected bond distances (Å) and bond angles (°) for compound **3** (Mn₃GdNa).

Bond Lengths around Manganese(1)		Bond Angles around Manganese(1)		O(11)-Gd(1)-O(15)	65.8(3)
N(1)-Mn(1)	2.014(11)	O(3)-Mn(1)-O(2)	173.6(4)	O(3)-Gd(1)-O(15)	75.7(3)
N(4)-Mn(1)	2.254(10)	O(3)-Mn(1)-O(21)	89.4(4)	O(20)-Gd(1)-O(15)	146.2(3)
O(2)-Mn(1)	1.907(9)	O(2)-Mn(1)-O(21)	96.5(4)	O(7)-Gd(1)-O(15)	121.2(3)
O(3)-Mn(1)	1.872(8)	O(3)-Mn(1)-N(1)	82.2(4)	O(22)-Gd(1)-O(15)	133.0(3)
O(16)-Mn(1)	2.194(9)	O(2)-Mn(1)-N(1)	91.7(4)	O(13)-Gd(1)-O(15)	77.2(3)
O(21)-Mn(1)	1.973(8)	O(21)-Mn(1)-N(1)	170.3(4)	O(14)-Gd(1)-O(15)	72.6(3)
Bond Lengths around Manganese(2)		O(3)-Mn(1)-O(16)	92.3(4)	Bond Angles around Sodium	
N(4)-Mn(2)	2.340(10)	O(2)-Mn(1)-O(16)	89.8(3)	O(2)-Na(1)-O(6)	91.8(4)
O(6)-Mn(2)	1.901(9)	O(21)-Mn(1)-O(16)	93.2(3)	O(2)-Na(1)-O(1)	65.9(3)
O(7)-Mn(2)	1.896(8)	N(1)-Mn(1)-O(16)	92.0(4)	O(6)-Na(1)-O(1)	110.2(4)
O(17)-Mn(2)	2.166(8)	O(3)-Mn(1)-N(4)	89.2(4)	O(2)-Na(1)-O(10)	98.1(3)
O(21)-Mn(2)	1.907(8)	O(2)-Mn(1)-N(4)	89.0(4)	O(6)-Na(1)-O(10)	115.9(3)
N(2)-Mn(2)	1.994(10)	O(21)-Mn(1)-N(4)	84.4(3)	O(1)-Na(1)-O(10)	131.6(4)
Bond Lengths around Manganese(3)		N(1)-Mn(1)-N(4)	90.6(4)	O(2)-Na(1)-O(5)	140.0(4)
N(3)-Mn(3)	2.011(10)	O(16)-Mn(1)-N(4)	177.2(4)	O(6)-Na(1)-O(5)	66.1(3)
O(10)-Mn(3)	1.889(9)	Bond Angles around Manganese(2)		O(1)-Na(1)-O(5)	89.9(4)
O(15)-Mn(3)	2.357(9)	O(7)-Mn(2)-O(6)	175.5(4)	O(10)-Na(1)-O(5)	121.3(4)
O(11)-Mn(3)	1.878(8)	O(7)-Mn(2)-O(21)	90.3(4)	O(2)-Na(1)-O(9)	103.8(4)
O(18)-Mn(3)	2.133(9)	O(6)-Mn(2)-O(21)	93.8(4)	O(6)-Na(1)-O(9)	164.1(4)
O(21)-Mn(3)	1.931(8)	O(7)-Mn(2)-N(2)	84.4(4)	O(1)-Na(1)-O(9)	74.5(3)
Bond Lengths around Gadolinium		O(6)-Mn(2)-N(2)	91.3(4)	O(10)-Na(1)-O(9)	65.2(3)
O(3)-Gd(1)	2.311(8)	O(21)-Mn(2)-N(2)	169.6(4)	O(5)-Na(1)-O(9)	99.3(4)
O(7)-Gd(1)	2.393(8)	O(7)-Mn(2)-O(17)	92.9(4)	O(2)-Na(1)-O(21)	66.7(3)
O(11)-Gd(1)	2.309(8)	O(6)-Mn(2)-O(17)	88.0(4)	O(6)-Na(1)-O(21)	63.5(3)
O(13)-Gd(1)	2.467(9)	O(21)-Mn(2)-O(17)	102.1(3)	O(1)-Na(1)-O(21)	131.8(4)
O(14)-Gd(1)	2.470(9)	N(2)-Mn(2)-O(17)	87.1(4)	O(10)-Na(1)-O(21)	63.5(3)
O(15)-Gd(1)	2.691(9)	O(7)-Mn(2)-N(4)	89.3(4)	O(5)-Na(1)-O(21)	122.7(3)
O(20)-Gd(1)	2.320(10)	O(6)-Mn(2)-N(4)	89.4(4)	O(9)-Na(1)-O(21)	125.4(3)
O(21)-Gd(1)	2.838(8)	O(21)-Mn(2)-N(4)	83.5(3)	Bond Angles containing Manganese and Gadolinium	
O(22)-Gd(1)	2.444(9)	N(2)-Mn(2)-N(4)	87.5(4)	Mn(1)-O(3)-Gd(1)	114.5(4)
Bond Lengths around		O(17)-Mn(2)-N(4)	173.9(3)	Mn(2)-O(7)-Gd(1)	112.2(4)
		Bond Angles around Manganese(3)		Mn(3)-O(11)-Gd(1)	105.9(3)
		O(11)-Mn(3)-O(10)	172.7(4)	Mn(3)-O(15)-Gd(1)	82.9(3)
		O(11)-Mn(3)-O(21)	90.5(4)	Mn(2)-O(21)-Gd(1)	95.6(3)
		O(10)-Mn(3)-O(21)	94.6(4)	Mn(3)-O(21)-Gd(1)	87.1(3)
		O(11)-Mn(3)-N(3)	83.1(4)	Mn(1)-O(21)-Gd(1)	92.5(3)
		O(10)-Mn(3)-N(3)	91.3(4)		
		O(21)-Mn(3)-N(3)	172.0(4)		

Sodium	O(11)-Mn(3)-O(18) 94.4(4)	Bond Angles containing Manganese and Sodium
O(1)-Na(1) 2.404(10)	O(10)-Mn(3)-O(18) 90.1(4)	
O(2)-Na(1) 2.328(10)	O(21)-Mn(3)-O(18) 98.1(3)	
O(5)-Na(1) 2.437(10)	N(3)-Mn(3)-O(18) 87.1(4)	
O(6)-Na(1) 2.341(10)	O(11)-Mn(3)-O(15) 79.6(3)	
O(9)-Na(1) 2.543(11)	O(10)-Mn(3)-O(15) 96.1(3)	
O(10)-Na(1) 2.405(10)	O(21)-Mn(3)-O(15) 79.7(3)	
O(21)-Na(1) 2.873(9)	N(3)-Mn(3)-O(15) 94.4(4)	
	O(18)-Mn(3)-O(15) 173.5(3)	
		Mn(1)-O(2)-Na(1) 108.3(4)
		Mn(3)-O(10)-Na(1) 102.2(4)
		Mn(2)-O(21)-Na(1) 91.9(3)
		Mn(3)-O(21)-Na(1) 86.4(3)
		Mn(1)-O(21)-Na(1) 88.5(3)
Bond Lengths containing Sodium and Manganese	Bond Angles around Gadolinium	Bond Angles containing Manganese(1), Manganese(2) and Manganese(3)
Na(1)-Mn(3) 3.359(5)	O(11)-Gd(1)-O(3) 123.1(3)	
Na(1)-Mn(1) 3.441(6)	O(11)-Gd(1)-O(20) 147.4(3)	
Na(1)-Mn(2) 3.501(5)	O(3)-Gd(1)-O(20) 82.5(3)	
	O(11)-Gd(1)-O(7) 84.6(3)	
Bond Lengths containing Manganese-Manganese	O(3)-Gd(1)-O(7) 81.2(3)	Mn(1)-N(4)-Mn(2) 85.4(3)
	O(20)-Gd(1)-O(7) 79.6(3)	Mn(2)-O(21)-Mn(3) 119.3(4)
Mn(1)-Mn(2) 3.115(3)	O(11)-Gd(1)-O(22) 74.6(3)	Mn(2)-O(21)-Mn(1) 106.8(4)
Mn(1)-Mn(3) 3.590(3)	O(3)-Gd(1)-O(22) 150.5(3)	Mn(3)-O(21)-Mn(1) 133.8(4)
Mn(2)-Mn(3) 3.312(3)	O(20)-Gd(1)-O(22) 74.2(3)	
	O(7)-Gd(1)-O(22) 77.1(3)	
Bond Lengths containing Manganese- Gadolinium	O(11)-Gd(1)-O(13) 85.5(3)	
	O(3)-Gd(1)-O(13) 125.4(3)	
Mn(1)-Gd(1) 3.526(2)	O(20)-Gd(1)-O(13) 95.5(3)	
Mn(2)-Gd(1) 3.571(2)	O(7)-Gd(1)-O(13) 152.3(3)	
Mn(3)-Gd(1) 3.351(2)	O(22)-Gd(1)-O(13) 75.4(3)	
	O(11)-Gd(1)-O(14) 126.4(3)	
Bond Length containing Sodium- Gadolinium	O(3)-Gd(1)-O(14) 74.2(3)	
	O(20)-Gd(1)-O(14) 76.8(3)	
	O(7)-Gd(1)-O(14) 147.8(3)	
	O(22)-Gd(1)-O(14) 116.4(3)	
	O(13)-Gd(1)-O(14) 52.7(3)	
Na(1)-Gd(1) 5.697(5)		

Table S5. Selected bond distances (Å) and bond angles (°) for compound **4(Mn₃NdNa)**.

Bond Lengths around Manganese(1)	Bond Angles around Manganese(1)	O(19)-Nd(1)-O(21) 129.5(2)
N(2)-Mn(1) 1.995(8)	O(7)-Mn(1)-O(6) 175.4(3)	O(7)-Nd(1)-O(21) 60.37(19)
N(4)-Mn(1) 2.337(8)	O(7)-Mn(1)-O(21) 91.3(3)	O(22)-Nd(1)-O(21) 121.5(2)
O(6)-Mn(1) 1.898(6)	O(6)-Mn(1)-O(21) 93.0(3)	O(17)-Nd(1)-O(21) 121.6(2)
O(7)-Mn(1) 1.870(6)	O(7)-Mn(1)-N(2) 83.7(3)	O(18)-Nd(1)-O(21) 132.8(2)
O(16)-Mn(1) 2.163(7)	O(6)-Mn(1)-N(2) 91.8(3)	O(14)-Nd(1)-O(21) 59.07(17)
	O(21)-Mn(1)-N(2) 169.3(3)	Bond Angles around Sodium

O(21)-Mn(1) 1.919(6)	O(7)-Mn(1)-O(16) 92.3(3)	O(6)-Na(1)-O(2) 92.2(3)
Bond Lengths around Manganese(2)	O(6)-Mn(1)-O(16) 88.4(3)	O(6)-Na(1)-O(10) 116.1(3)
N(3)-Mn(2) 2.024(7)	O(21)-Mn(1)-O(16) 102.3(2)	O(2)-Na(1)-O(10) 98.3(3)
O(11)-Mn(2) 1.871(6)	N(2)-Mn(1)-O(16) 87.4(3)	O(6)-Na(1)-O(5) 66.7(3)
O(10)-Mn(2) 1.882(6)	O(7)-Mn(1)-N(4) 89.3(3)	O(2)-Na(1)-O(5) 140.8(3)
O(14)-Mn(2) 2.355(7)	O(6)-Mn(1)-N(4) 89.6(3)	O(10)-Na(1)-O(5) 120.4(3)
O(15)-Mn(2) 2.144(7)	O(21)-Mn(1)-N(4) 83.1(2)	O(6)-Na(1)-O(1) 110.0(3)
O(21)-Mn(2) 1.941(5)	N(2)-Mn(1)-N(4) 87.4(3)	O(2)-Na(1)-O(1) 66.1(3)
Bond Lengths around Manganese(3)	O(16)-Mn(1)-N(4) 174.3(3)	O(10)-Na(1)-O(1) 131.8(3)
O(21)-Mn(3) 1.974(6)	Bond Angles around Manganese(2)	O(5)-Na(1)-O(1) 89.7(3)
O(13)-Mn(3) 2.200(7)	O(11)-Mn(2)-O(10) 172.5(3)	O(6)-Na(1)-O(9) 164.2(3)
O(3)-Mn(3) 1.874(6)	O(11)-Mn(2)-O(21) 91.4(3)	O(2)-Na(1)-O(9) 103.2(3)
N(4)-Mn(3) 2.256(7)	O(10)-Mn(2)-O(21) 94.5(3)	O(10)-Na(1)-O(9) 65.3(2)
N(1)-Mn(3) 2.013(8)	O(11)-Mn(2)-N(3) 82.1(3)	O(5)-Na(1)-O(9) 98.7(3)
O(2)-Mn(3) 1.892(6)	O(10)-Mn(2)-N(3) 91.6(3)	O(1)-Na(1)-O(9) 74.2(3)
Bond Lengths around Neodymium	O(21)-Mn(2)-N(3) 172.1(3)	O(6)-Na(1)-O(21) 63.8(2)
O(3)-Nd(1) 2.348(6)	O(11)-Mn(2)-O(15) 94.0(3)	O(2)-Na(1)-O(21) 66.5(2)
O(7)-Nd(1) 2.457(6)	O(10)-Mn(2)-O(15) 89.8(3)	O(10)-Na(1)-O(21) 63.9(2)
O(11)-Nd(1) 2.356(6)	O(21)-Mn(2)-O(15) 97.8(2)	O(5)-Na(1)-O(21) 123.3(3)
O(19)-Nd(1) 2.368(7)	N(3)-Mn(2)-O(15) 87.2(3)	O(1)-Na(1)-O(21) 131.8(3)
O(14)-Nd(1) 2.752(7)	O(11)-Mn(2)-O(14) 80.9(3)	O(9)-Na(1)-O(21) 125.5(2)
O(18)-Nd(1) 2.516(6)	O(10)-Mn(2)-O(14) 95.5(3)	Bond Angles containing Manganese and Neodymium
O(17)-Nd(1) 2.513(7)	O(21)-Mn(2)-O(14) 80.0(2)	Mn(3)-O(3)-Nd(1) 114.6(3)
O(21)-Nd(1) 2.881(6)	N(3)-Mn(2)-O(14) 94.4(3)	Mn(1)-O(7)-Nd(1) 112.4(3)
O(22)-Nd(1) 2.498(7)	O(15)-Mn(2)-O(14) 174.4(3)	Mn(2)-O(11)-Nd(1) 105.9(3)
Bond Lengths around Sodium	Bond Angles around Manganese(3)	Mn(2)-O(14)-Nd(1) 82.6(2)
O(21)-Na(1) 2.854(7)	O(3)-Mn(3)-O(2) 173.3(3)	Mn(1)-O(21)-Nd(1) 95.4(2)
O(10)-Na(1) 2.406(7)	O(3)-Mn(3)-O(21) 90.2(3)	Mn(2)-O(21)-Nd(1) 86.88(19)
O(9)-Na(1) 2.551(8)	O(2)-Mn(3)-O(21) 96.3(3)	Mn(3)-O(21)-Nd(1) 92.4(2)
O(6)-Na(1) 2.319(8)	O(3)-Mn(3)-N(1) 82.3(3)	Bond Angles containing Manganese and Sodium
O(5)-Na(1) 2.422(9)	O(2)-Mn(3)-N(1) 91.1(3)	Mn(1)-O(21)-Na(1) 91.9(2)
O(2)-Na(1) 2.337(8)	O(21)-Mn(3)-N(1) 171.1(3)	Mn(2)-O(21)-Na(1) 86.5(2)
O(1)-Na(1) 2.425(8)	O(3)-Mn(3)-O(13) 92.0(3)	Mn(3)-O(21)-Na(1) 88.8(2)
Bond Lengths containing Sodium and Manganese	O(2)-Mn(3)-O(13) 89.4(3)	Mn(2)-O(10)-Na(1) 102.1(3)
	O(21)-Mn(3)-O(13) 93.4(2)	Mn(1)-O(6)-Na(1) 111.4(3)
	N(1)-Mn(3)-O(13) 91.6(3)	Mn(3)-O(2)-Na(1) 108.2(3)
	O(3)-Mn(3)-N(4) 89.7(3)	Bond Angles containing Manganese(1), Manganese(2) and Manganese(3)
	O(2)-Mn(3)-N(4) 89.2(3)	
	O(21)-Mn(3)-N(4) 84.1(3)	
	N(1)-Mn(3)-N(4) 91.2(3)	
	O(13)-Mn(3)-N(4) 176.9(3)	
	Bond Angles around	

Na(1)-Mn(1) 3.491(4)	Neodymium		
Na(1)-Mn(2) 3.352(4)	O(3)-Nd(1)-O(11)	121.8(2)	Mn(3)-N(4)-Mn(1) 85.9(2)
Na(1)-Mn(3) 3.436(4)	O(3)-Nd(1)-O(19)	83.3(2)	Mn(1)-O(21)-Mn(2) 119.1(3)
	O(11)-Nd(1)-O(19)	147.7(3)	Mn(1)-O(21)-Mn(3) 107.0(3)
Bond Lengths containing Manganese-Manganese	O(3)-Nd(1)-O(7)	81.1(2)	Mn(2)-O(21)-Mn(3) 133.7(3)
	O(11)-Nd(1)-O(7)	83.9(2)	
Mn(1)-Mn(2) 3.329(2)	O(19)-Nd(1)-O(7)	80.2(2)	
Mn(1)-Mn(3) 3.129(2)	O(3)-Nd(1)-O(22)	151.5(2)	
Mn(2)-Mn(3) 3.601(2)	O(11)-Nd(1)-O(22)	75.2(2)	
	O(19)-Nd(1)-O(22)	74.1(3)	
Bond Lengths containing Manganese- Neodymium	O(7)-Nd(1)-O(22)	78.2(2)	
	O(3)-Nd(1)-O(17)	74.9(2)	
Mn(1)-Nd(1) 3.61 (2)	O(11)-Nd(1)-O(17)	126.0(2)	
Mn(2)-Nd(1) 3.385(2)	O(19)-Nd(1)-O(17)	77.2(3)	
Mn(3)-Nd(1) 3.561(2)	O(7)-Nd(1)-O(17)	148.7(2)	
	O(22)-Nd(1)-O(17)	115.4(3)	
Bond Length containing Sodium- Neodymium	O(3)-Nd(1)-O(18)	124.9(2)	
	O(11)-Nd(1)-O(18)	85.4(2)	
	O(19)-Nd(1)-O(18)	96.5(3)	
	O(7)-Nd(1)-O(18)	153.5(2)	
	O(22)-Nd(1)-O(18)	75.7(3)	
	O(17)-Nd(1)-O(18)	51.9(2)	
	O(3)-Nd(1)-O(14)	74.6(2)	
	O(11)-Nd(1)-O(14)	65.0(2)	
	O(19)-Nd(1)-O(14)	146.9(2)	
	O(7)-Nd(1)-O(14)	119.3(2)	
	O(22)-Nd(1)-O(14)	133.0(2)	
	O(17)-Nd(1)-O(14)	73.4(2)	
	O(18)-Nd(1)-O(14)	77.1(2)	
	O(3)-Nd(1)-O(21)	61.85(19)	
	O(11)-Nd(1)-O(21)	61.85(17)	