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Table S23. Bond distances (Å) and angles (°) for complex **9**.

Mn1 - O1	2.116(4)	N2 - C14	1.392(6)
Mn1 - O2	2.119(3)	C1 - C2	1.433(9)
Mn1 - N1	2.088(5)	C1 - C6	1.409(9)
Mn1 - N2	2.440(4)	C2 - C3	1.373(11)
Mn1 - N2'	2.104(4)	C3 - C4	1.360(12)
Na1 - O2	2.598(4)	C4 - C5	1.404(11)
Na1 - O3	2.387(5)	C5 - C6	1.390(9)
Na1 - O4	2.265(4)	C6 - C7	1.530(8)
Na1 - N1	2.444(4)	C7 - C21	1.515(7)
Na2 - O1	2.386(5)	C8 - C9	1.404(9)
Na2 - O2	2.265(4)	C8 - C13	1.434(8)
Na2 - O5	2.484(6)	C9 - C10	1.379(10)
Na2 - O6	2.355(5)	C10 - C11	1.374(9)
O1 - C1	1.317(7)	C11 - C12	1.388(9)
O2 - C20	1.338(6)	C12 - C13	1.388(8)
O3 - C31	1.402(8)	C14 - C15	1.480(9)
O3 - C32	1.398(8)	C14 - C22	1.354(8)
O4 - C33	1.415(10)	C15 - C16	1.393(8)
O4 - C34	1.398(9)	C15 - C20	1.408(7)
O5 - C35	1.409(10)	C16 - C17	1.386(9)
O5 - C36	1.370(11)	C17 - C18	1.387(10)
O6 - C37	1.370(13)	C18 - C19	1.379(9)
O6 - C38	1.378(10)	C19 - C20	1.403(9)
N1 - C7	1.445(7)	C32 - C33	1.501(11)
N1 - C8	1.381(7)	C36 - C37	1.420(14)
N2 - C13	1.451(8)		

N2 - Mn1 - N2'	96.0(1)	Mn1 - N1 - C7	119.4(3)
N1 - Mn1 - N2'	138.2(2)	C7 - N1 - C8	117.5(4)
N1 - Mn1 - N2	74.3(1)	Mn1 - N2 - C14	111.8(3)
O2 - Mn1 - N2'	108.7(1)	Mn1 - N2 - C13	102.2(3)
O2 - Mn1 - N2	82.7(1)	C13 - N2 - C14	114.0(4)
O2 - Mn1 - N1	110.2(1)	O1 - C1 - C6	123.9(5)
O1 - Mn1 - N2'	108.7(1)	O1 - C1 - C2	118.4(5)
O1 - Mn1 - N2	154.7(1)	C2 - C1 - C6	117.7(5)
O1 - Mn1 - N1	90.1(1)	C1 - C2 - C3	120.4(6)
O1 - Mn1 - O2	84.2(1)	C2 - C3 - C4	122.1(7)
O4 - Na1 - N1	153.6(2)	C3 - C4 - C5	118.6(7)
O3 - Na1 - N1	102.3(2)	C4 - C5 - C6	121.6(6)
O3 - Na1 - O4	72.2(2)	C1 - C6 - C5	119.6(5)
O2 - Na1 - N1	86.3(1)	C5 - C6 - C7	117.3(5)
O2 - Na1 - O4	99.1(2)	C1 - C6 - C7	123.1(5)
O2 - Na1 - O3	171.1(2)	N1 - C7 - C6	111.6(4)
O5 - Na2 - O6	68.2(2)	C6 - C7 - C21	111.0(4)
O2 - Na2 - O6	179.7(2)	N1 - C7 - C21	114.7(4)
O2 - Na2 - O5	112.0(2)	N1 - C8 - C13	116.8(5)
O1 - Na2 - O6	104.5(2)	N1 - C8 - C9	127.0(5)
O1 - Na2 - O5	154.0(2)	C9 - C8 - C13	116.2(5)
O1 - Na2 - O2	75.2(1)	C8 - C9 - C10	121.3(5)
Mn1 - O1 - Na2	91.8(1)	C9 - C10 - C11	122.0(6)
Na2 - O1 - C1	108.3(3)	C10 - C11 - C12	118.6(5)
Mn1 - O1 - C1	121.7(3)	C11 - C12 - C13	120.8(5)
Na1 - O2 - Na2	117.8(1)	C8 - C13 - C12	121.0(5)
Mn1 - O2 - Na2	95.1(1)	N2 - C13 - C12	120.6(5)
Mn1 - O2 - Na1	79.6(1)	N2 - C13 - C8	118.4(4)
Na2 - O2 - C20	123.7(3)	N2 - C14 - C22	125.3(5)
Na1 - O2 - C20	108.1(2)	N2 - C14 - C15	115.2(5)
Mn1 - O2 - C20	124.8(3)	Na1 - C14 - C22	76.1(3)

Table S23. Bond distances (Å) and angles (°) for complex **9** (cont.)

Na1	- O3	- C32	109.7(4)	Na1	- C14	- C15	100.0(3)
Na1	- O3	- C31	120.5(3)	C15	- C14	- C22	119.4(5)
C31	- O3	- C32	112.3(5)	C14	- C15	- C20	120.0(5)
Na1	- O4	- C34	120.4(4)	C14	- C15	- C16	120.2(5)
Na1	- O4	- C33	112.5(4)	C16	- C15	- C20	119.6(5)
C33	- O4	- C34	112.7(5)	C15	- C16	- C17	121.2(5)
Na2	- O5	- C36	113.9(5)	C16	- C17	- C18	119.3(5)
Na2	- O5	- C35	132.1(4)	C17	- C18	- C19	120.3(6)
C35	- O5	- C36	112.6(6)	C18	- C19	- C20	121.3(5)
Na2	- O6	- C38	123.0(4)	C15	- C20	- C19	118.1(5)
Na2	- O6	- C37	116.3(5)	O2	- C20	- C19	120.0(4)
C37	- O6	- C38	116.6(6)	O2	- C20	- C15	121.8(5)
Mn1	- N1	- Na1	83.9(2)	O3	- C32	- C33	108.0(6)
Na1	- N1	- C8	109.4(3)	O4	- C33	- C32	108.6(6)
Na1	- N1	- C7	105.1(3)	O5	- C36	- C37	114.2(8)
Mn1	- N1	- C8	114.7(3)	O6	- C37	- C36	115.8(8)

Prime denotes a transformation of -x, -y, 1-z.

Table S24. Bond distances (Å) and angles (°) for complex **14**.

Mn1	- O1	1.859(8)	C5	- C6	1.427(16)
Mn1	- O2	1.841(8)	C6	- C7	1.434(14)
Mn1	- O3	2.205(8)	C8	- C9	1.400(14)
Mn1	- N1	1.961(8)	C8	- C13	1.394(15)
Mn1	- N2	1.983(8)	C9	- C10	1.404(16)
I1	- I2	2.996(1)	C10	- C11	1.375(19)
I2	- I3	2.857(1)	C11	- C12	1.368(16)
O1	- C1	1.310(14)	C12	- C13	1.392(15)
O2	- C20	1.330(14)	C14	- C15	1.429(15)
O3	- C21	1.418(16)	C15	- C16	1.409(17)
O3	- C24	1.416(16)	C15	- C20	1.403(15)
O4	- C25	1.36(3)	C16	- C17	1.362(18)
O4	- C28	1.37(3)	C17	- C18	1.366(19)
N1	- C7	1.320(12)	C18	- C19	1.39(2)
N1	- C8	1.432(12)	C19	- C20	1.408(16)
N2	- C13	1.400(13)	C21	- C22	1.419(20)
N2	- C14	1.308(14)	C22	- C23	1.51(2)
C1	- C2	1.391(16)	C23	- C24	1.513(20)
C1	- C6	1.407(15)	C25	- C26	1.46(3)
C2	- C3	1.364(18)	C26	- C27	1.47(4)
C3	- C4	1.381(18)	C27	- C28	1.44(4)
C4	- C5	1.359(17)			

N1	- Mn1 - N2	81.5(3)	C1	- C6 - C7	123.3(10)
O3	- Mn1 - N2	90.2(3)	N1	- C7 - C6	124.2(9)
O3	- Mn1 - N1	89.4(3)	N1	- C8 - C13	114.5(8)
O2	- Mn1 - N2	93.3(3)	N1	- C8 - C9	124.8(8)
O2	- Mn1 - N1	173.3(3)	C9	- C8 - C13	120.6(9)
O2	- Mn1 - O3	94.9(3)	C8	- C9 - C10	117.9(10)
O1	- Mn1 - N2	172.5(3)	C9	- C10 - C11	120.9(10)
O1	- Mn1 - N1	92.8(3)	C10	- C11 - C12	120.9(11)
O1	- Mn1 - O3	94.5(3)	C11	- C12 - C13	119.9(11)
O1	- Mn1 - O2	92.1(3)	C8	- C13 - C12	119.7(10)
I1	- I2 - I3	177.5(1)	N2	- C13 - C12	125.5(10)
Mn1	- O1 - C1	129.8(7)	N2	- C13 - C8	114.7(9)
Mn1	- O2 - C20	129.9(7)	N2	- C14 - C15	125.7(10)
Mn1	- O3 - C24	125.5(7)	C14	- C15 - C20	123.6(10)
Mn1	- O3 - C21	123.7(7)	C14	- C15 - C16	117.2(10)
C21	- O3 - C24	109.7(10)	C16	- C15 - C20	119.1(10)
C25	- O4 - C28	113.4(18)	C15	- C16 - C17	121.7(11)
Mn1	- N1 - C8	113.7(6)	C16	- C17 - C18	119.0(12)
Mn1	- N1 - C7	125.7(7)	C17	- C18 - C19	121.9(12)
C7	- N1 - C8	120.6(8)	C18	- C19 - C20	119.8(11)
Mn1	- N2 - C14	123.8(7)	C15	- C20 - C19	118.5(10)
Mn1	- N2 - C13	114.1(7)	O2	- C20 - C19	118.5(10)
C13	- N2 - C14	122.0(9)	O2	- C20 - C15	123.0(10)
O1	- C1 - C6	124.0(10)	O3	- C21 - C22	110.5(12)
O1	- C1 - C2	118.3(10)	C21	- C22 - C23	106.6(12)
C2	- C1 - C6	117.6(10)	C22	- C23 - C24	105.3(13)
C1	- C2 - C3	121.6(11)	O3	- C24 - C23	106.6(11)
C2	- C3 - C4	120.4(12)	O4	- C25 - C26	103.2(19)
C3	- C4 - C5	120.9(11)	C25	- C26 - C27	104.4(19)
C4	- C5 - C6	119.0(10)	C26	- C27 - C28	104.7(20)
C1	- C6 - C5	120.2(10)	O4	- C28 - C27	106(2)
C5	- C6 - C7	116.4(9)			

Table S25. Bond distances (Å) and angles (°) for complex **16**.

Mn1	- Mn1'	2.715(1)	C10	- C11	1.382(8)
Mn1	- O1	1.926(3)	C11	- C12	1.386(7)
Mn1	- O2'	1.921(4)	C12	- C13	1.382(7)
Mn1	- O3	1.808(4)	C14	- C15	1.399(6)
Mn1	- O3'	1.806(3)	C15	- C16	1.435(10)
Mn1	- N1	2.035(5)	C15	- C20	1.432(8)
Mn1	- N2'	2.036(5)	C16	- C17	1.340(7)
O1	- C1	1.302(6)	C17	- C18	1.409(8)
O2	- C20	1.297(7)	C17	- C29	1.540(10)
N1	- C7	1.305(7)	C18	- C19	1.395(10)
N1	- C8	1.434(7)	C19	- C20	1.412(6)
N2	- C13	1.425(6)	C19	- C33	1.545(8)
N2	- C14	1.307(8)	C21	- C22	1.515(8)
C1	- C2	1.426(7)	C21	- C23	1.522(13)
C1	- C6	1.417(8)	C21	- C24	1.525(9)
C2	- C3	1.380(8)	C25	- C26	1.471(13)
C2	- C21	1.544(8)	C25	- C27	1.467(15)
C3	- C4	1.421(10)	C25	- C28	1.489(13)
C4	- C5	1.348(8)	C29	- C30	1.499(10)
C4	- C25	1.525(10)	C29	- C31	1.446(10)
C5	- C6	1.415(8)	C29	- C32	1.512(11)
C6	- C7	1.427(7)	C33	- C34	1.531(10)
C8	- C9	1.385(6)	C33	- C35	1.527(10)
C8	- C13	1.399(8)	C33	- C36	1.510(10)
C9	- C10	1.397(7)			

N1	- Mn1 - N2'	175.3(2)	C10	- C11 - C12	120.9(5)
O3'	- Mn1 - N2'	92.2(2)	C11	- C12 - C13	120.3(5)
O3'	- Mn1 - N1	90.9(2)	C8	- C13 - C12	119.9(5)
O3	- Mn1 - N2'	90.7(2)	N2	- C13 - C12	119.0(5)
O3	- Mn1 - N1	93.2(2)	N2	- C13 - C8	121.0(4)
O3	- Mn1 - O3'	82.6(1)	N2	- C14 - C15	129.4(5)
O2'	- Mn1 - N2'	89.9(2)	C14	- C15 - C20	123.5(6)
O2'	- Mn1 - N1	86.4(2)	C14	- C15 - C16	117.3(4)
O2'	- Mn1 - O3'	93.3(2)	C16	- C15 - C20	119.1(5)
O2'	- Mn1 - O3	175.9(1)	C15	- C16 - C17	123.2(5)
O1	- Mn1 - N2'	87.2(2)	C16	- C17 - C29	124.9(5)
O1	- Mn1 - N1	90.1(2)	C16	- C17 - C18	116.5(6)
O1	- Mn1 - O3'	174.6(2)	C18	- C17 - C29	118.5(5)
O1	- Mn1 - O3	92.0(2)	C17	- C18 - C19	124.3(5)
O1	- Mn1 - O2'	92.1(1)	C18	- C19 - C33	120.1(5)
Mn1	- O1 - C1	133.1(3)	C18	- C19 - C20	118.7(5)
Mn1'	- O2 - C20	133.8(3)	C20	- C19 - C33	121.0(5)
Mn1	- O3 - Mn1'	97.4(2)	C15	- C20 - C19	118.0(5)
Mn1	- N1 - C8	120.5(3)	O2	- C20 - C19	121.6(4)
Mn1	- N1 - C7	123.2(3)	O2	- C20 - C15	120.3(5)
C7	- N1 - C8	115.7(4)	C2	- C21 - C24	111.7(5)
Mn1'	- N2 - C14	122.7(3)	C2	- C21 - C23	109.5(5)
Mn1'	- N2 - C13	120.4(4)	C2	- C21 - C22	109.1(5)
C13	- N2 - C14	116.7(4)	C23	- C21 - C24	108.4(6)
O1	- C1 - C6	121.6(5)	C22	- C21 - C24	108.2(6)
O1	- C1 - C2	120.6(4)	C22	- C21 - C23	110.0(5)
C2	- C1 - C6	117.8(5)	C4	- C25 - C28	111.7(8)
C1	- C2 - C21	120.7(5)	C4	- C25 - C27	109.1(7)
C1	- C2 - C3	118.1(5)	C4	- C25 - C26	113.3(6)
C3	- C2 - C21	121.2(5)	C27	- C25 - C28	106.1(7)
C2	- C3 - C4	124.5(5)	C26	- C25 - C28	109.8(7)
C3	- C4 - C25	119.4(5)	C26	- C25 - C27	106.5(9)

Table S25. Bond distances (Å) and angles (°) for complex **16** (cont.)

C3	- C4	- C5	116.6(5)	C17	- C29	- C32	109.2(6)
C5	- C4	- C25	123.9(5)	C17	- C29	- C31	110.9(6)
C4	- C5	- C6	122.1(5)	C17	- C29	- C30	111.2(6)
C1	- C6	- C5	120.8(5)	C31	- C29	- C32	108.5(7)
C5	- C6	- C7	116.0(4)	C30	- C29	- C32	107.6(6)
C1	- C6	- C7	123.1(5)	C30	- C29	- C31	109.4(7)
N1	- C7	- C6	128.6(5)	C19	- C33	- C36	112.9(6)
N1	- C8	- C13	121.3(4)	C19	- C33	- C35	107.0(5)
N1	- C8	- C9	119.5(5)	C19	- C33	- C34	111.1(5)
C9	- C8	- C13	119.1(5)	C35	- C33	- C36	108.9(6)
C8	- C9	- C10	121.4(5)	C34	- C33	- C36	107.2(6)
C9	- C10	- C11	118.5(5)	C34	- C33	- C35	109.8(6)

Prime denotes a transformation of -x, -y, -z.

Magnetic properties of dimeric manganese complexes.

Magnetic susceptibilities data for the starting compounds **1-4** were collected in the temperature range 1.9-300 K and the temperature dependence of the magnetic moments are typical of weakly coupled Mn(II) dimers. The effective magnetic moments observed at room temperature fall around 5.9 μ_B, as expected for weakly interacting Mn(II) centers. The data of **3**, taken as representative of the four compounds (**1-4**), were fitted with the simple theoretical equation[1] obtained by the Heisenberg spin hamiltonian $H_{ex} = -2J\hat{S}_1 \cdot \hat{S}_2$, with $S_1 = S_2 = 5/2$. To obtain a good fitting, we included a correction for a small quantity of monomeric Mn(II) impurities which were assumed to obey Curie law. The following equation is therefore obtained for the total susceptibility $\chi = \frac{1}{2}(1-x)\chi_{\mathrm{dim}} + x\frac{Ng^2\mu_B^2 S(S+1)}{3kT}$, where S and g are the spin and the g factor of the impurity (assumed to be the same of the Mn (II) ion in the dimer), and x the monomeric impurity fraction. A good fit to the collected data was obtained for $g = 1.97$, $J = -4.7$ cm^{-1}, and $x = 1.8$ %, see Figure S10. The observed coupling constant fall in the typical range for μ-phenoxo Mn(II) dimers.[2]

The temperature dependence of the magnetic moment of compounds **5-8** also indicates antiferromagnetically coupled Mn(II) dimers. As the behaviour of the *t*-butyl derivatives **7** and **8** are essentially identical to those of **5** and **6**, only the temperature dependence of the magnetic moment of the latter two compounds are discussed. The data were fitted again with equation (1), and the best fitting values are $g = 2.02$, $J = -43.0$ cm^{-1}, $x = 3.9$ % and $g = 1.97$, $J = -40.8$ cm^{-1}, $x = 0.4$ %, respectively for **5** and **6**, see Figures S11 and S12. The exchange constant values found for **5-8** show fairly strong antiferromagnetic coupling for these μ-amido Mn(II) dimers. It is worth noting that these values are higher than those observed for μ-hydroxo, μ-alkoxo, μ-phenoxo and μ-carboxilato Mn(II)-Mn(II) dimers (with exchange coupling constants of few cm^{-1}) intensively studied[3,4,5,6] within the investigation of inorganic model complexes of manganese-containing metalloproteins.[3]The temperature dependence of the magnetic moment of **15** and its *t*-butyl derivative **16** are quite similar and indicate antiferromagnetically coupled Mn(IV) dimers. The data were fitted using a Heisenberg Hamiltonian, with $S_1 = S_2 = 3/2$, and including a correction for monomeric Mn(IV) impurities, and those for **16** are reported in Figure S13. The best fitting values are $g = 1.86$, $J = -80.1$ cm^{-1}, $x = 1.8$ %. The antiferromagnetic coupling constant obtained for these bis μ-oxo Mn(IV) dimers are similar to those observed for other bis μ-oxo Mn(IV) Schiff base dimers (usually *ca* 100 cm^{-1}) with comparable Mn-Mn distance.[3,7]

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Figure S10. Magnetic susceptibility (o; 10^{-3} cm^3mol^{-1}) and effective magnetic moment (•, μ_B) *per* Mn for **3** as a function of the temperature. The solid and dashed lines are the best theoretical fits (see text) to the experimental data.

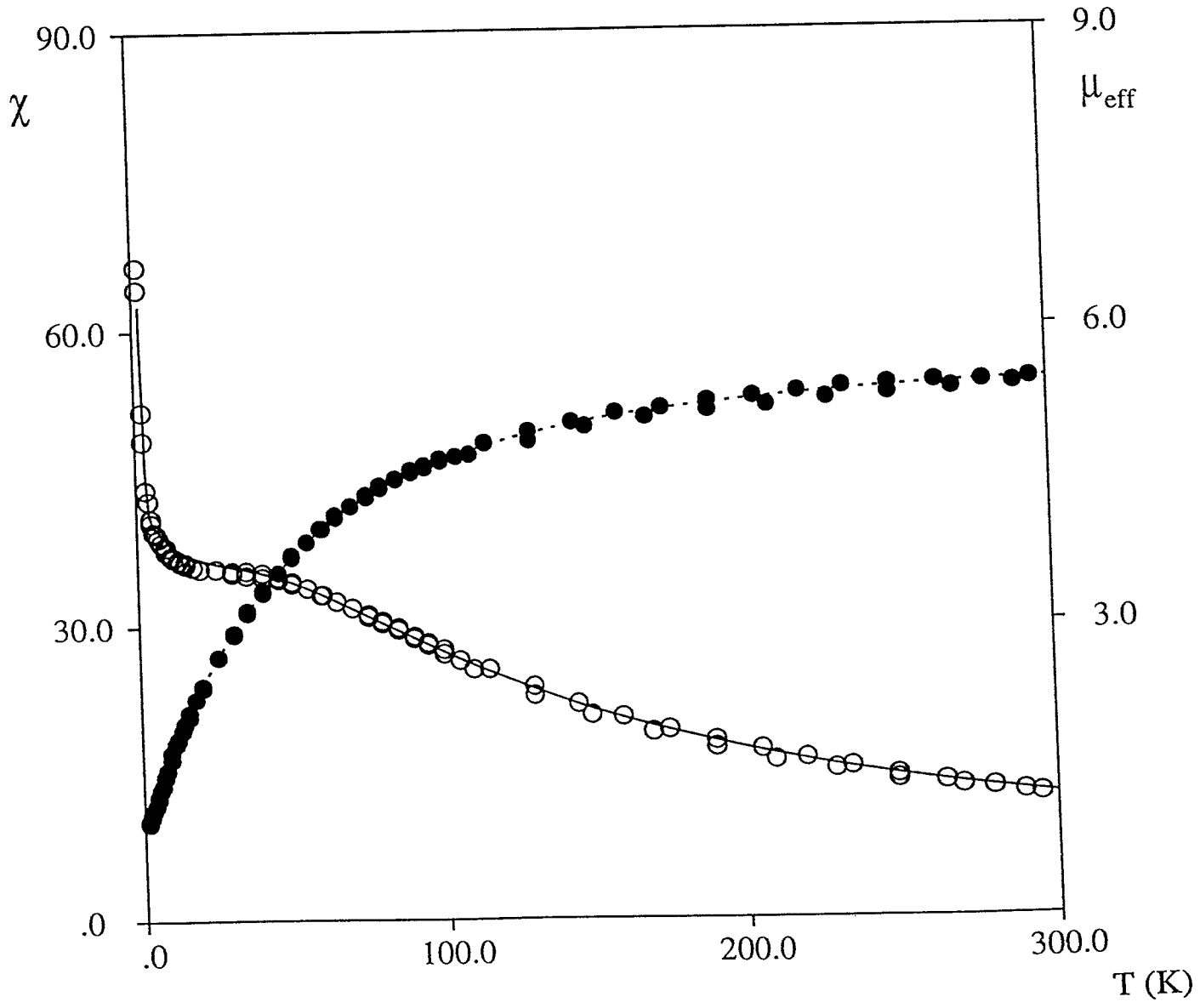

Figure S11. Magnetic susceptibility (o; 10^{-3} cm^3mol^{-1}) and effective magnetic moment (•, μ_B) *per* Mn for **5** as a function of the temperature. The solid and dashed lines are the best theoretical fits (see text) to the experimental data.

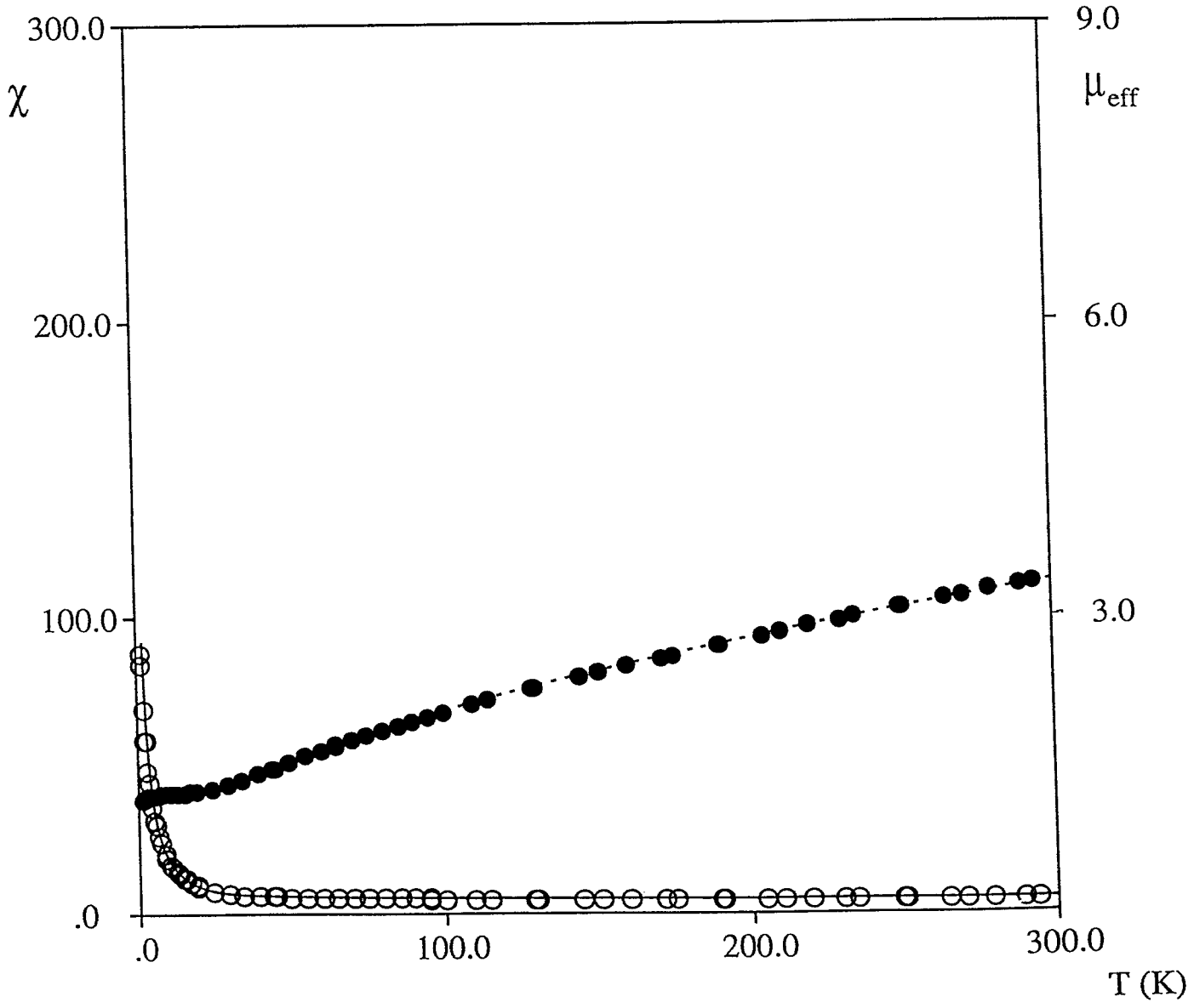

Figure S12. Magnetic susceptibility (o; 10^{-3} cm^3mol^{-1}) and effective magnetic moment (•, μ_B) *per* Mn for **6** as a function of the temperature. The solid and dashed lines are the best theoretical fits (see text) to the experimental data.

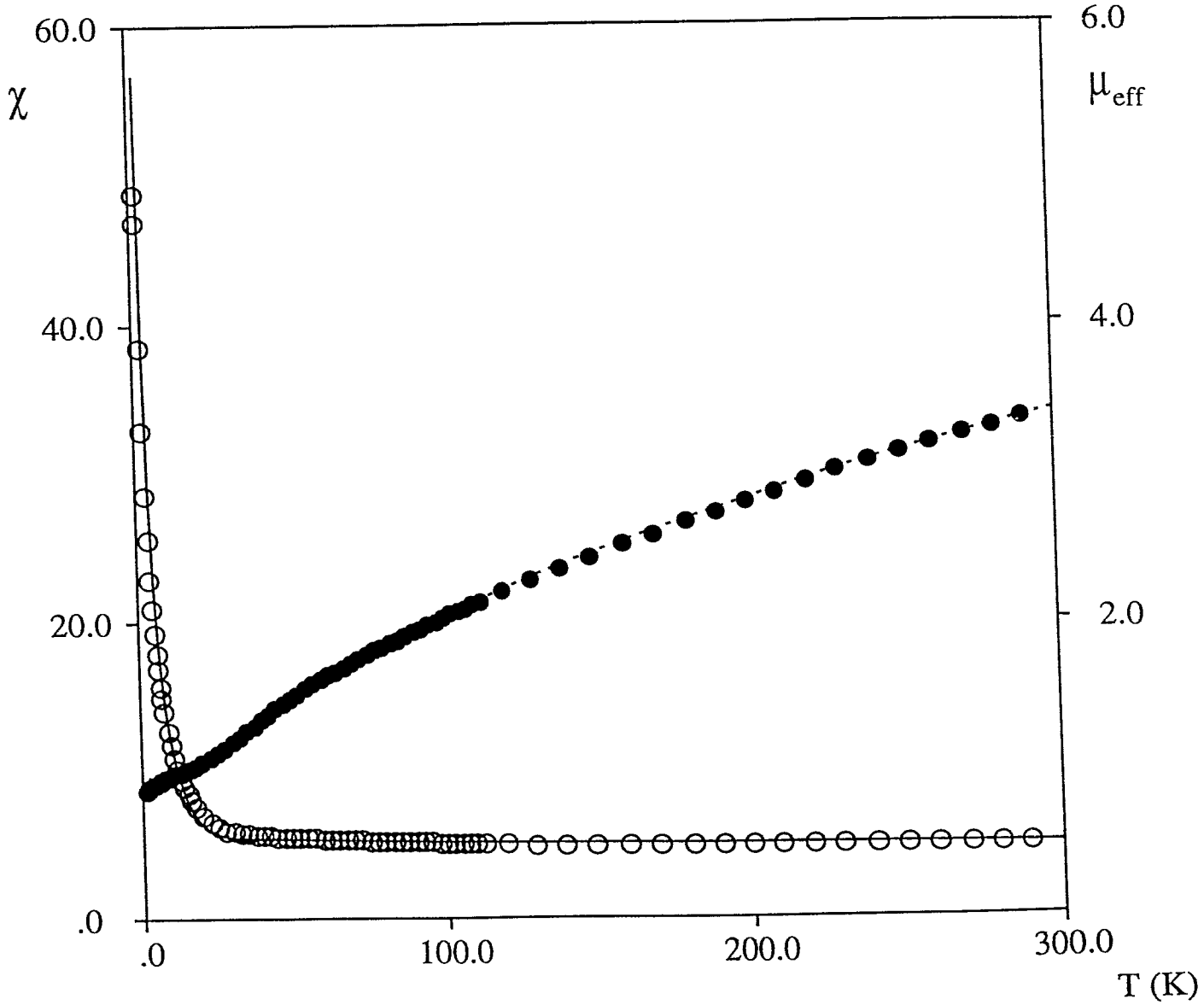

Figure S13. Magnetic susceptibility (o; 10^{-3} cm^3mol^{-1}) and effective magnetic moment (•, μ_B) *per* Mn for **16** as a function of the temperature. The solid and dashed lines are the best theoretical fits (see text) to the experimental data.