Supporting Information for

A Highly-flexible Cyclic-decavanadate Ligand for Interconversion of Dinuclear- and Trinuclear-cobalt(II) and Manganese(II) Cores

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Table S1. Crystallographic Data for **Co3**

	Co3	**Mn3**[41]
formula	$C_{48}H_{114}Co_3N_8O_{33}V_{10}$	$C_{48}H_{114}Mn_3N_8O_{33}V_{10}$
fw	2017.66	2005.69
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	15.8703(9)	15.9731(14)
b (Å)	26.0327(14)	26.127(2)
c (Å)	19.7604(11)	19.7628(17)
α (deg)	90	90
β (deg)	92.1531(18)	91.538(2)
γ (deg)	90	90
V / (Å^3)	8158.2(8)	8244.5(13)
Z	4	4
temp. (K)	83(2)	83(2)
GOF	1.084	1.150
$R1$ [$I > 2\sigma(I)$]	0.0398	0.0550
$wR2$ [$I > 2\sigma(I)$]	0.1036	0.1358

$R1 = \sum||F_o| - |F_c|/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **Co3** and the Reported Isostructural Trimanganese Containing Polyoxovanadate (**Mn3**)[41]

	$[M_3(OAc)(H_2O)V_{10}O_{30}]^{5-}$	
	Co3 (M = Co)	**Mn3** (M = Mn)
	Bond Length (Å)	
M1···M2	3.2734(6)	3.4499(7)
M1···M3	3.3194(5)	3.4866(7)
M2···M3	3.0035(7)	3.1349(7)
M1–O	2.049(2)–2.174(2)	2.110(2)–2.272(2)
M2–O	2.027(2)-2.167(2)	2.095(2)–2.257(2)
M3–O	2.000(2)–2.214(2)	2.069(2)–2.351(2)
	Bond Angle (deg)	
M1–O10–M2	99.97(7)	101.08(9)
M1–O19–M2	97.86(6)	99.23(9)
M2–O4–M3	92.66(7)	93.21(9)
M2–O19–M3	87.36(6)	88.22(8)
M3–O19–M1	99.29(7)	101.00(9)
M3–O31–M1	100.99(7)	101.31(9)

Table S3. EXAFS fit parameters for **Mn2** and **Mn3**

	EXAFS (solid)			EXAFS (solution)		
	CN[a]	r^b / Å	$\sigma^{2\,c}$ / Å^2	CN[a]	r^b / Å	$\sigma^{2\,c}$ / Å^2
Compound Mn2						
Mn–O	6[d]	2.16(1)	0.008(1)	4.6(9)	2.15(1)	0.006(2)
Mn···Mn	1[d]	3.2(1)	0.018(4)	1[d]	3.20(9)	0.013(3)
Mn···V	6[d]	3.45(7)	0.018(4)[e]	4.6[f]	3.50(4)	0.013(3)[e]
Compound Mn3						
Mn–O	3[d]	2.07(3)	0.001(1)	3(2)	2.05(8)	0.01(1)
Mn–O	3[d]	2.22(3)	0.001(5)	3(2)[f]	2.20(7)	0.01(2)
Mn···Mn	0.667[d]	3.1(2)	0.01(4)	0.667[e]	3.1(1)	0.005(6)
Mn···Mn	1.333[d]	3.4(2)[g]	0.01(4)[h]	1.333[d]	3.4(1)[g]	0.005(6)[h]
Mn···V	4[d]	3.4(4)	0.01(1)	4.36[i]	3.5(8)	0.01(1)

[a]Coordination number. [b]Distances between Mn and O, Mn, and V. [c]Debye-Waller factor. [d]The coordination numbers are fixed according th the values from single X-ray study. [e]The Debye-Waller factor was kept equal to that of the Mn–Mn. [f]The CN was kept equal to that of the Mn–O. [g]Δr was kept equal to that of another Mn–Mn. [h]The Debye-Waller factor was kept equal to that of another Mn–Mn. [i]The CN was fixed to four-thirds of CN of Mn–O.

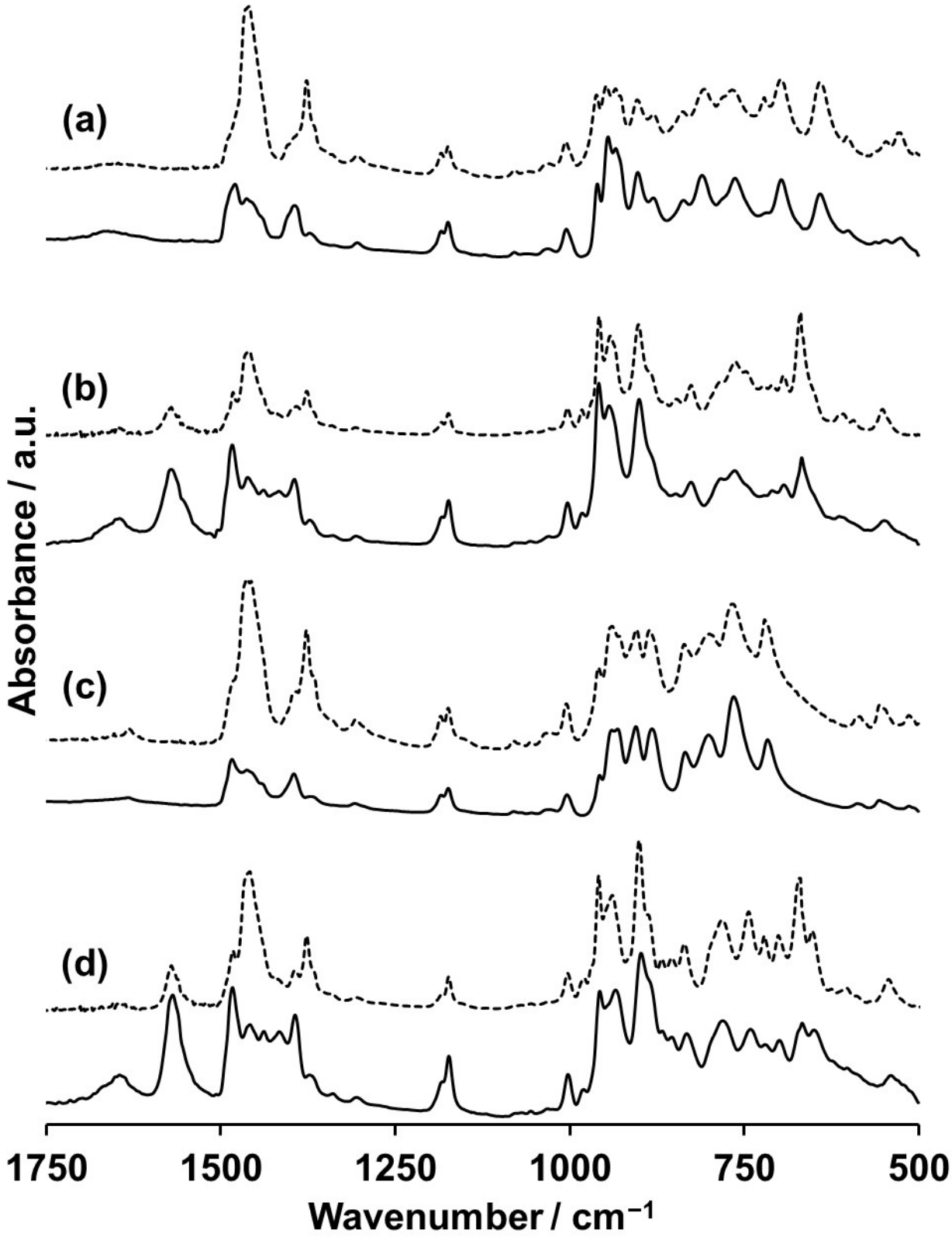

Figure S1. IR spectra of (a) **Co2**, (b) **Co3**, (c) **Mn2**, and (d) **Mn3**. Solid line: ATR method. Dotted line: Nujol-mull method.

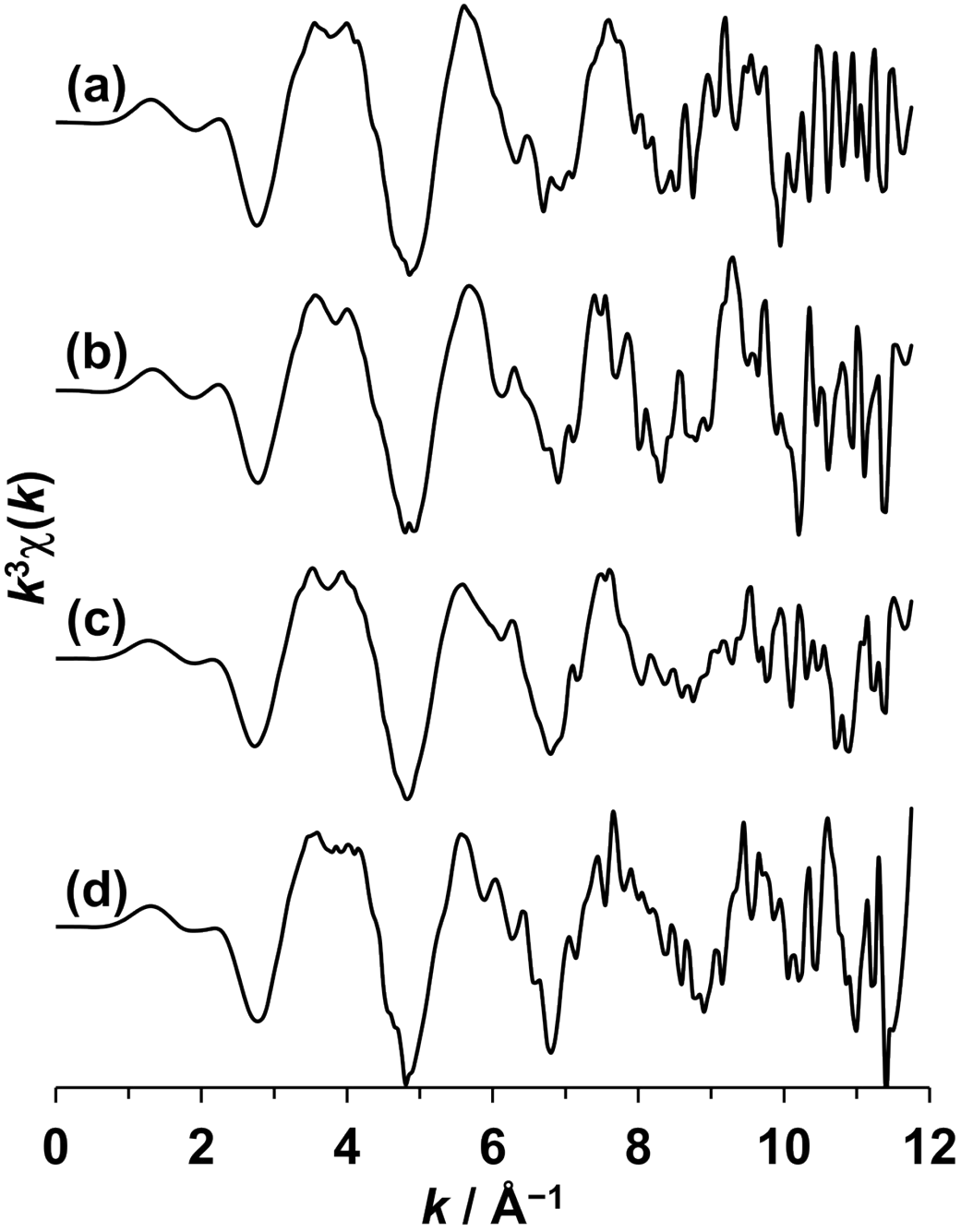

Figure S2. Mn K-edge EXAFS oscillations of **Mn2** (a) in BN pellets and (b) in propylene carbonate, and **Mn3** (c) in BN pelets and (d) in propylene carboncate.