

**Mononuclear transition metal cymantrenecarboxylates as precursors for spinel-type  
manganites**

Pavel S. Koroteev, Andrey B. Ilyukhin, Andrey V. Gavrikov, Konstantin A. Babeshkin,  
Nikolay N. Efimov

*N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of  
Sciences, Leninsky prosp. 31, 119991 Moscow, GSP-1, Russian Federation,  
pskoroteev@list.ru*

**SUPPLEMENTARY MATERIALS**

**Table S1.** Selected bond lengths [Å] and angles [°] for complexes **1-8**.

	<b>1</b> (M=Co)	<b>2</b> (M=Ni)	<b>3</b> (M=Zn)
M(1)-O(11)	2.1212(10)	2.0828(11)	2.169(2)
M(1)-O(12)	2.1319(11)	2.0896(11)	2.173(2)
M(1)-O(13)	2.0883(11)	2.0474(11)	2.121(2)
M(1)-O(14)	2.0830(12)	2.0469(11)	2.115(2)
M(1)-O(15)	2.0704(12)	2.0467(12)	2.120(2)
M(1)-O(16)	2.0752(11)	2.0552(12)	2.129(2)
Mn(1)-C(2)	2.1384(14)	2.1404(14)	2.143(3)
Mn(1)-C(3)	2.1430(16)	2.1401(15)	2.145(3)
Mn(1)-C(4)	2.1437(16)	2.1414(16)	2.140(3)
Mn(1)-C(5)	2.1439(16)	2.1433(15)	2.143(3)
Mn(1)-C(6)	2.1415(15)	2.1394(14)	2.135(3)
Mn(1)-C(13)	1.7971(17)	1.7961(17)	1.794(3)
Mn(1)-C(14)	1.7867(18)	1.7915(18)	1.790(4)
Mn(1)-C(15)	1.7936(18)	1.7920(17)	1.792(3)
Mn(2)-C(8)	2.1336(14)	2.1328(13)	2.129(3)
Mn(2)-C(9)	2.1395(15)	2.1405(14)	2.139(3)
Mn(2)-C(10)	2.1526(16)	2.1526(15)	2.153(3)
Mn(2)-C(11)	2.1543(15)	2.1554(15)	2.150(3)
Mn(2)-C(12)	2.1459(15)	2.1438(14)	2.143(3)
Mn(2)-C(16)	1.8045(16)	1.8056(16)	1.804(3)
Mn(2)-C(17)	1.8009(18)	1.8020(17)	1.804(3)
Mn(2)-C(18)	1.7886(17)	1.7872(17)	1.785(3)
O(11)-M(1)-O(12)	86.35(4)	87.96(4)	85.71(8)

O(11)-M(1)-O(13)	89.02(5)	89.33(5)	90.09(8)
O(11)-M(1)-O(14)	95.87(5)	94.39(5)	96.91(8)
O(11)-M(1)-O(15)	89.94(5)	89.51(5)	89.76(9)
O(11)-M(1)-O(16)	174.27(5)	176.40(5)	172.46(9)
O(12)-M(1)-O(13)	96.50(5)	96.10(5)	97.05(8)
O(12)-M(1)-O(14)	89.72(5)	90.49(5)	90.59(8)
O(12)-M(1)-O(15)	174.81(5)	176.24(5)	174.24(9)
O(12)-M(1)-O(16)	88.86(5)	89.27(5)	87.54(9)
O(13)-M(1)-O(14)	172.33(5)	172.54(5)	170.02(8)
O(13)-M(1)-O(15)	87.05(5)	86.64(5)	86.50(9)
O(13)-M(1)-O(16)	88.41(5)	88.68(5)	87.40(8)
O(14)-M(1)-O(15)	87.05(5)	86.94(5)	86.42(8)
O(14)-M(1)-O(16)	87.24(5)	87.93(5)	86.52(9)
O(15)-M(1)-O(16)	95.04(6)	93.38(6)	97.17(10)

#### 4

Co(1)-O(1)	1.9776(19)
Co(1)-O(6)	1.9586(19)
Co(1)-N(1)	2.011(2)
Co(1)-N(3)	2.019(2)
Mn(1)-C(2)	2.120(3)
Mn(1)-C(3)	2.128(3)
Mn(1)-C(4)	2.137(3)
Mn(1)-C(5)	2.144(3)
Mn(1)-C(6)	2.136(3)
Mn(1)-C(7)	1.793(3)
Mn(1)-C(8)	1.787(3)
Mn(1)-C(9)	1.787(3)
Mn(2)-C(11)	2.128(3)
Mn(2)-C(12)	2.136(3)
Mn(2)-C(13)	2.136(3)
Mn(2)-C(14)	2.135(3)
Mn(2)-C(15)	2.132(3)
Mn(2)-C(16)	1.799(3)
Mn(2)-C(17)	1.795(3)
Mn(2)-C(18)	1.790(4)
O(6)-Co(1)-O(1)	129.77(9)
O(6)-Co(1)-N(1)	106.46(9)
O(1)-Co(1)-N(1)	97.44(9)

O(6)-Co(1)-N(3)	99.51(9)
O(1)-Co(1)-N(3)	110.18(9)
N(1)-Co(1)-N(3)	113.97(10)

## 5

Co(1)-O(1)	2.0374(16)
Co(1)-N(1)	2.1512(19)
Co(1)-N(2)	2.1519(18)
Mn(1)-C(2)	2.147(2)
Mn(1)-C(3)	2.147(2)
Mn(1)-C(4)	2.134(3)
Mn(1)-C(5)	2.140(3)
Mn(1)-C(6)	2.145(2)
Mn(1)-C(7)	1.791(3)
Mn(1)-C(8)	1.786(3)
Mn(1)-C(9)	1.795(3)

O(1)#1-Co(1)-O(1)	89.35(9)
O(1)#1-Co(1)-N(1)	162.78(7)
O(1)-Co(1)-N(1)	91.87(7)
O(1)#1-Co(1)-N(1)#1	91.87(7)
O(1)-Co(1)-N(1)#1	162.78(7)
N(1)-Co(1)-N(1)#1	92.02(10)
O(1)#1-Co(1)-N(2)#1	101.18(7)
O(1)-Co(1)-N(2)#1	87.47(7)
N(1)-Co(1)-N(2)#1	96.03(7)
N(1)#1-Co(1)-N(2)#1	75.44(7)
O(1)#1-Co(1)-N(2)	87.47(7)
O(1)-Co(1)-N(2)	101.18(7)
N(1)-Co(1)-N(2)	75.44(7)
N(1)#1-Co(1)-N(2)	96.03(7)
N(2)#1-Co(1)-N(2)	167.91(10)

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#1 -x+1, y, -z+1/2

## 6

Ni(1)-O(1)	2.067(2)
Ni(1)-O(11)	2.072(3)
Ni(1)-N(1)	2.076(3)
Ni(1)-N(2)	2.097(3)

Ni(1)-N(3)	2.089(3)
Ni(1)-N(4)	2.079(3)
Mn(1)-C(2)	2.130(4)
Mn(1)-C(3)	2.148(4)
Mn(1)-C(4)	2.152(4)
Mn(1)-C(5)	2.146(4)
Mn(1)-C(6)	2.131(4)
Mn(1)-C(7)	1.787(5)
Mn(1)-C(8)	1.788(4)
Mn(1)-C(9)	1.785(4)
Mn(2)-C(11)	2.153(4)
Mn(2)-C(12)	2.140(4)
Mn(2)-C(13)	2.136(4)
Mn(2)-C(14)	2.137(4)
Mn(2)-C(15)	2.144(3)
Mn(2)-C(16)	1.790(4)
Mn(2)-C(17)	1.795(5)
Mn(2)-C(18)	1.776(4)

O(1)-Ni(1)-O(11)	91.91(10)
O(1)-Ni(1)-N(1)	87.93(11)
O(11)-Ni(1)-N(1)	167.18(11)
O(1)-Ni(1)-N(4)	91.54(11)
O(11)-Ni(1)-N(4)	94.04(11)
N(1)-Ni(1)-N(4)	98.78(11)
O(1)-Ni(1)-N(3)	169.64(11)
O(11)-Ni(1)-N(3)	89.88(11)
N(1)-Ni(1)-N(3)	92.57(11)
N(4)-Ni(1)-N(3)	78.15(12)
O(1)-Ni(1)-N(2)	89.37(11)
O(11)-Ni(1)-N(2)	88.89(11)
N(1)-Ni(1)-N(2)	78.29(12)
N(4)-Ni(1)-N(2)	176.90(12)
N(3)-Ni(1)-N(2)	100.87(11)

7

Cu(1)-O(1)	1.938(8)
Cu(1)-N(1)	1.971(10)
Mn(1)-C(2)	2.132(11)
Mn(1)-C(3)	2.125(12)

Mn(1)-C(4)	2.120(12)
Mn(1)-C(5)	2.123(12)
Mn(1)-C(6)	2.119(13)
Mn(1)-C(7)	1.794(17)
Mn(1)-C(8)	1.768(18)
Mn(1)-C(9)	1.782(16)

O(1)-Cu(1)-O(1)#1	180.0
O(1)-Cu(1)-N(1)#1	89.1(4)
O(1)#1-Cu(1)-N(1)#1	90.9(4)
O(1)-Cu(1)-N(1)	90.8(4)
O(1)#1-Cu(1)-N(1)	89.2(4)
N(1)#1-Cu(1)-N(1)	180.0

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#1 -x+1, -y, -z+1

## 8

Cu(1)-O(1)	1.946(3)
Cu(1)-O(6)	1.983(3)
Cu(1)-O(11)	2.215(3)
Cu(1)-N(1)	2.021(4)
Cu(1)-N(2)	2.017(4)
Mn(1)-C(2)	2.125(4)
Mn(1)-C(3)	2.130(5)
Mn(1)-C(4)	2.156(5)
Mn(1)-C(5)	2.156(5)
Mn(1)-C(6)	2.141(5)
Mn(1)-C(7)	1.792(5)
Mn(1)-C(8)	1.785(5)
Mn(1)-C(9)	1.791(5)
Mn(2)-C(11)	2.134(5)
Mn(2)-C(12)	2.148(5)
Mn(2)-C(13)	2.155(5)
Mn(2)-C(14)	2.143(5)
Mn(2)-C(15)	2.130(5)
Mn(2)-C(16)	1.801(6)
Mn(2)-C(17)	1.803(5)
Mn(2)-C(18)	1.792(6)

O(1)-Cu(1)-O(6)	91.29(14)
O(1)-Cu(1)-N(2)	171.93(15)
O(6)-Cu(1)-N(2)	92.42(15)
O(1)-Cu(1)-N(1)	95.25(15)
O(6)-Cu(1)-N(1)	167.71(15)
N(2)-Cu(1)-N(1)	79.84(16)
O(1)-Cu(1)-O(11)	90.37(14)
O(6)-Cu(1)-O(11)	93.75(14)
N(2)-Cu(1)-O(11)	96.53(14)
N(1)-Cu(1)-O(11)	96.59(14)

**Table S2.** H-bonds in the structures of compounds **1-4** and **6-8** [lengths, Å and angles, °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
<b>1</b>				
O(11)-H(1)...O(17)	0.71(2)	2.03(2)	2.7334(16)	169(2)
O(11)-H(2)...O(2) (-x, -y, -z)	0.82(2)	1.91(2)	2.7227(16)	179(2)
O(12)-H(3)...O(1) (-x, -y, -z)	0.83(3)	1.89(3)	2.6993(15)	163(3)
O(12)-H(4)...O(19) (-x+1, -y, -z)	0.87(2)	1.88(2)	2.7427(17)	170(2)
O(13)-H(5)...O(17) (x+1, y, z)	0.84(2)	1.89(2)	2.7305(16)	172(2)
O(13)-H(6)...O(4) (x+1, y, z)	0.79(2)	2.05(2)	2.8318(15)	171(2)
O(14)-H(7)...O(3)	0.80(2)	1.97(2)	2.7682(16)	176(2)
O(14)-H(8)...O(19) (-x, -y, -z)	0.71(2)	2.00(2)	2.7102(16)	171(3)
O(15)-H(9)...O(11) (-x, -y+1, -z)	0.74(2)	2.16(2)	2.8870(16)	167(2)
O(15)-H(10)...O(4)	0.79(3)	1.96(3)	2.7444(17)	174(3)
O(16)-H(11)...O(20)	0.79(2)	1.95(2)	2.7312(18)	170(2)
O(16)-H(12)...O(3) (x+1, y, z)	0.80(2)	1.96(2)	2.7594(17)	174.6(19)
O(17)-H(13)...O(2) (-x-1, -y, -z)	0.81(2)	2.08(2)	2.8575(16)	160(2)
O(17)-H(14)...O(4) (-x-1, -y+1, -z)	0.77(3)	1.94(3)	2.6998(15)	169(3)
O(18)-H(15)...O(3) (x+1, y, z)	0.77(2)	1.98(2)	2.7496(16)	172(2)
O(18)-H(16)...O(1)	0.85(3)	1.98(3)	2.8178(17)	172(3)
O(19)-H(17)...O(20) (x+1, y, z)	0.83(2)	1.87(2)	2.6826(18)	164(2)
O(19)-H(18)...O(12) (x+1, y, z)	0.78(2)	2.11(2)	2.8726(17)	166(2)
O(20)-H(19)...O(18) (x-1, y, z)	0.72(3)	1.97(3)	2.668(2)	164(3)
O(20)-H(20)...O(1)	0.83(3)	2.00(3)	2.8028(18)	162(2)
<b>2</b>				
O(11)-H(1)...O(17)	0.74(2)	2.01(2)	2.7278(15)	166(2)
O(11)-H(2)...O(2) (-x, -y, -z)	0.81(2)	1.92(2)	2.7260(15)	177(2)
O(12)-H(3)...O(1) (-x, -y, -z)	0.85(2)	1.90(2)	2.7337(16)	169(2)

O(12)-H(4)...O(19) (-x+1, -y, -z)	0.78(3)	1.94(3)	2.6999(16)	163(2)
O(13)-H(5)...O(17) (x+1, y, z)	0.73(2)	1.99(2)	2.7174(16)	174(2)
O(13)-H(6)...O(4) (x+1, y, z)	0.80(2)	2.03(2)	2.8245(15)	174(2)
O(14)-H(7)...O(3)	0.73(2)	1.99(2)	2.7044(16)	169(2)
O(14)-H(8)...O(19) (-x, -y, -z)	0.85(2)	1.92(2)	2.7688(16)	172(2)
O(15)-H(9)...O(11) (-x, -y+1, -z)	0.76(3)	1.99(3)	2.7474(16)	176(2)
O(15)-H(10)...O(4)	0.80(2)	2.10(2)	2.8846(16)	167(2)
O(16)-H(11)...O(20)	0.79(2)	1.98(2)	2.7739(16)	176.6(19)
O(16)-H(12)...O(3) (x+1, y, z)	0.78(3)	1.97(3)	2.7334(17)	165(3)
O(17)-H(13)...O(2) (-x-1, -y, -z)	0.80(2)	2.10(2)	2.8505(15)	157(2)
O(17)-H(14)...O(4) (-x-1, -y+1, -z)	0.78(2)	1.93(2)	2.6952(15)	170(2)
O(18)-H(15)...O(3) (x+1, y, z)	0.73(3)	2.02(3)	2.7471(17)	174(3)
O(18)-H(16)...O(1)	0.82(2)	1.99(3)	2.8102(17)	172(2)
O(19)-H(17)...O(20) (x+1, y, z)	0.83(3)	1.84(3)	2.6696(18)	174(3)
O(19)-H(18)...O(12) (x+1, y, z)	0.75(3)	2.17(3)	2.8894(17)	160(2)
O(20)-H(19)...O(18) (x-1, y, z)	0.84(3)	2.02(3)	2.8009(17)	155(2)
O(20)-H(20)...O(1)	0.71(3)	1.97(3)	2.6649(19)	168(3)

### 3

O(11)-H(1)...O(17)	0.90	1.83	2.717(3)	169
O(11)-H(2)...O(2) (-x, -y, -z)	0.90	1.88	2.742(3)	161
O(12)-H(3)...O(1) (-x, -y, -z)	0.90	1.84	2.737(3)	171
O(12)-H(4)...O(19) (-x+1, -y, -z)	0.90	1.80	2.693(3)	170
O(13)-H(5)...O(17) (x+1, y, z)	0.90	1.92	2.814(3)	175
O(13)-H(6)...O(4) (x+1, y, z)	0.90	1.84	2.734(3)	174
O(14)-H(7)...O(3)	0.90	1.86	2.753(3)	171
O(14)-H(8)...O(19) (-x, -y, -z)	0.90	1.81	2.696(3)	168
O(15)-H(9)...O(11) (-x, -y+1, -z)	0.90	1.85	2.745(3)	177
O(15)-H(10)...O(4)	0.90	2.05	2.887(3)	154
O(16)-H(11)...O(20)	0.90	1.84	2.723(3)	168
O(16)-H(12)...O(3) (x+1, y, z)	0.90	1.87	2.762(3)	174
O(17)-H(13)...O(2) (-x-1, -y, -z)	0.90	1.84	2.701(3)	159
O(17)-H(14)...O(4) (-x-1, -y+1, -z)	0.90	2.00	2.855(3)	157
O(18)-H(15)...O(3) (x+1, y, z)	0.90	1.87	2.741(3)	162
O(18)-H(16)...O(1)	0.90	1.91	2.807(3)	176
O(19)-H(17)...O(20) (x+1, y, z)	0.90	2.00	2.875(3)	162
O(19)-H(18)...O(12) (x+1, y, z)	0.90	1.79	2.680(3)	169
O(20)-H(19)...O(18) (x-1, y, z)	0.90	1.80	2.673(3)	164
O(20)-H(20)...O(1)	0.90	1.97	2.807(3)	153

### 4

N(2)-H(1)...O(7) (-x, -y+1, -z)	0.91(3)	1.84(3)	2.736(3)	168(3)
N(4)-H(2)...O(2) (-x+1/2, y+1/2, -z+1/2)	0.94(4)	1.80(4)	2.722(3)	164(3)

### 6

O(11)-H(1)...O(2)	0.85(4)	1.79(4)	2.620(4)	165(4)
O(11)-H(2)...O(7)	0.78(4)	1.89(4)	2.657(4)	173(4)
O(12)-H(3)...O(13)	0.92(4)	1.86(4)	2.762(4)	165(4)
O(12)-H(4)...O(6)	0.78(4)	1.96(4)	2.723(4)	169(5)
O(13)-H(5)...O(7) (x, y, z-1)	0.73(4)	2.10(4)	2.825(4)	173(5)
O(13)-H(6)...O(12) (x, -y+1/2, z-1/2)	0.88(4)	1.82(4)	2.691(4)	168(4)
<b>7</b>				
N(2)-H(2A)...O(2) (x, -y+1/2, z-1/2)	0.86	1.93	2.79(2)	158
<b>8</b>				
O(11)-H(1)...O(7) (x, y+1, z)	0.77	1.96	2.714(5)	166
O(11)-H(2)...O(2) (x, y+1, z)	0.89	1.99	2.758(5)	144

**Table S3.** Structurally characterized mononuclear cymantrenecarboxylates of *d*-metals (CSD version 5.42 updates (Sep 2021)\*).

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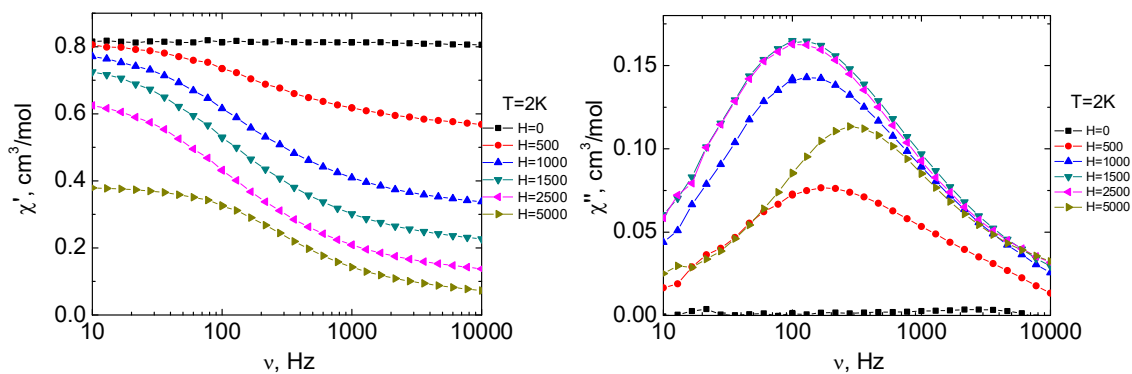
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\* Groom C. R., Bruno I. J., Lightfoot M. P., Ward S. C. The Cambridge Structural Database. *Acta Crystallographica Section B*. **2016**. V.72. №2. P. 171-179.

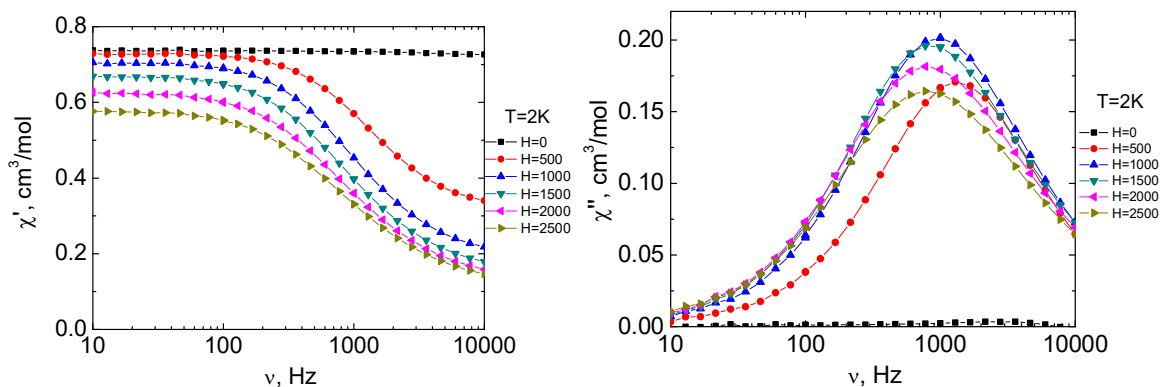
**Table S4.** Crystal data and structure refinement for complexes **1-8**.

Identification code	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>18</sub> H <sub>28</sub> CoMn <sub>2</sub> O <sub>20</sub>	C <sub>18</sub> H <sub>28</sub> Mn <sub>2</sub> NiO <sub>20</sub>	C <sub>18</sub> H <sub>28</sub> Mn <sub>2</sub> O <sub>20</sub> Zn	C <sub>24</sub> H <sub>16</sub> CoMn <sub>2</sub> N <sub>4</sub> O <sub>10</sub>
Formula weight	733.21	732.99	739.65	689.22
Temperature, K	173(2)	173(2)	173(2)	150(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P2 <sub>1</sub> /n
a, Å	6.4016(5)	6.3826(2)	6.4041(2)	13.9056(7)
b, Å	12.6294(9)	12.6104(3)	12.6715(5)	7.5358(4)
c, Å	18.5659(13)	18.5067(4)	18.6201(7)	26.8049(14)
α, °	93.005(3)	93.1140(10)	93.1270(10)	90
β, °	96.058(3)	95.9200(10)	95.7570(10)	103.165(2)
γ, °	103.604(3)	103.6810(10)	103.9860(10)	90
Volume, Å <sup>3</sup>	1446.12(18)	1434.79(6)	1453.96(9)	2735.1(2)
Z	2	2	2	4
D (calc), Mg/m <sup>3</sup>	1.684	1.697	1.689	1.674
μ, mm <sup>-1</sup>	1.511	1.601	1.757	1.571
F(000)	746	748	752	1380
Crystal size, mm	0.36 x 0.24 x 0.10	0.40 x 0.32 x 0.10	0.32 x 0.3 x 0.08	0.28 x 0.24 x 0.18
θ range, °	2.071, 33.256	2.220, 32.940	2.206, 33.002	2.478, 28.334
Index ranges	-9<=h<=9 -18<=k<=18 -28<=l<=28	-9<=h<=9 -18<=k<=18 -26<=l<=27	-9<=h<=9 -19<=k<=19 -28<=l<=28	-18<=h<=18 -10<=k<=10 -35<=l<=35
Reflections collected	17299	21786	22125	32727
Independent reflections, R <sub>int</sub>	9683, 0.0356	9755, 0.0328	9882, 0.0347	6806, 0.0505
Completeness to θ = 25.242°	99.8 %	99.9 %	99.9 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.7465, 0.4958	0.7465, 0.5444	0.7465, 0.5488	0.7457, 0.574
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9683 / 1 / 450	9755 / 0 / 450	9882 / 0 / 370	6806 / 0 / 376
Goodness-of-fit	1.004	1.037	1.121	1.015
R1, wR2 [I>2σ(I)]	0.0316, 0.0796	0.0314, 0.0789	0.0515, 0.1532	0.0398, 0.0950
R1, wR2 (all data)	0.0409, 0.0835	0.0410, 0.0829	0.0665, 0.1631	0.0611, 0.1048
Largest diff. peak and hole, e.Å <sup>-3</sup>	0.576, -0.413	0.608, -0.421	1.150, -2.073	0.614, -0.356

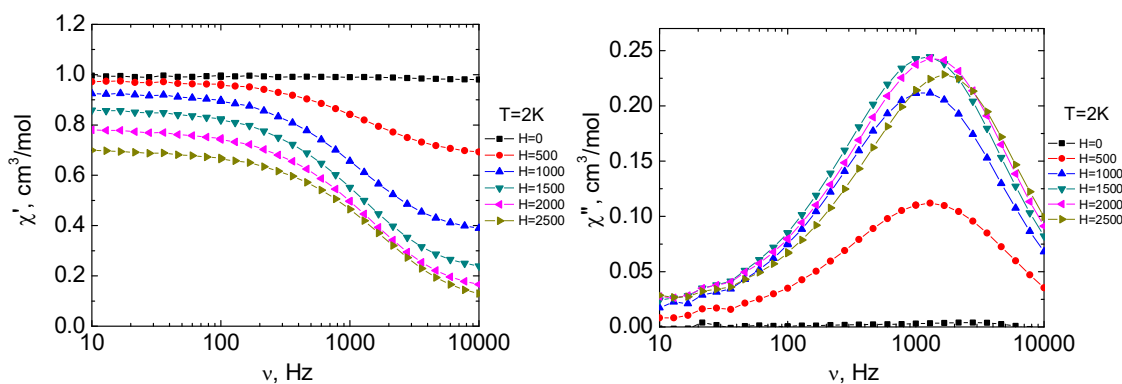
Identification code	5	6	7	8
Empirical formula	C <sub>52</sub> H <sub>40</sub> CoMn <sub>2</sub> N <sub>4</sub> O <sub>10</sub>	C <sub>41.50</sub> H <sub>34</sub> Mn <sub>2</sub> N <sub>4</sub> NiO <sub>13</sub>	C <sub>24</sub> H <sub>16</sub> CuMn <sub>2</sub> N <sub>4</sub> O <sub>10</sub>	C <sub>28</sub> H <sub>18</sub> CuMn <sub>2</sub> N <sub>2</sub> O <sub>11</sub>
Formula weight	1049.69	965.32	693.83	731.86
Temperature, K	150(2)	120(2)	296(2)	120(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a, Å	25.0607(13)	12.7133(17)	7.955(4)	15.5777(10)
b, Å	10.7040(5)	44.403(6)	14.956(8)	6.7135(4)
c, Å	18.4501(9)	7.2002(10)	11.228(6)	26.6800(17)
β, °	107.166(2)	101.017(3)	93.383(16)	91.316(2)
Volume, Å <sup>3</sup>	4728.8(4)	3989.7(9)	1333.5(12)	2789.5(3)
Z	4	4	2	4
D (calc), Mg/m <sup>3</sup>	1.474	1.607	1.728	1.743
μ, mm <sup>-1</sup>	0.937	1.164	1.786	1.714
F(000)	2148	1972	694	1468
Crystal size, mm	0.22 x 0.12 x 0.10	0.26 x 0.08 x 0.02	0.20 x 0.02 x 0.02	0.26 x 0.04 x 0.02
θ range, °	2.084, 27.919	2.135, 26.429	2.271, 25.396	2.291, 30.054
Index ranges	-32 ≤ h ≤ 32 -14 ≤ k ≤ 14 -24 ≤ l ≤ 24	-15 ≤ h ≤ 13 -55 ≤ k ≤ 55 -9 ≤ l ≤ 9	-9 ≤ h ≤ 9 0 ≤ k ≤ 18 -13 ≤ l ≤ 13	-21 ≤ h ≤ 21 -9 ≤ k ≤ 9 -37 ≤ l ≤ 37
Reflections collected	28267	28019	4851	56077
Independent reflections, R <sub>int</sub>	5643, 0.0556	8141, 0.0919	2442, 0.1272	8287, 0.0830
Completeness to θ = 25.242°	100.0 %	99.6 %	100.0 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.7456, 0.6283	0.7454, 0.6399	0.7452, 0.5738	0.7456, 0.6561
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5643 / 42 / 328	8141 / 42 / 605	2442 / 0 / 187	8287 / 0 / 398
Goodness-of-fit	0.965	1.004	1.156	1.086
R1, wR2 [I > 2σ(I)]	0.0397, 0.1092	0.0499, 0.0822	0.1029, 0.2360	0.0550, 0.1522
R1, wR2 (all data)	0.0585, 0.1235	0.1040, 0.0958	0.1885, 0.2673	0.0736, 0.1644
Largest diff. peak and hole, e.Å <sup>-3</sup>	1.015, -0.311	0.535, -0.470	1.925, -0.549	2.098, -0.893



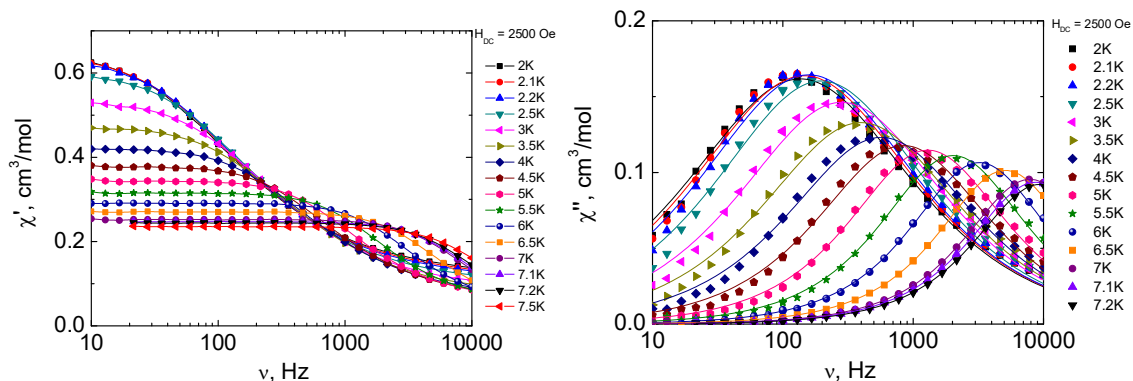
**Figure S1.** Frequency dependencies of the real,  $\chi'$  (left) and imaginary,  $\chi''$  (right) components of dynamic magnetic susceptibility for complex **1** at  $T = 2$  K under various dc magnetic fields (Oe). Solid lines are visual guides.



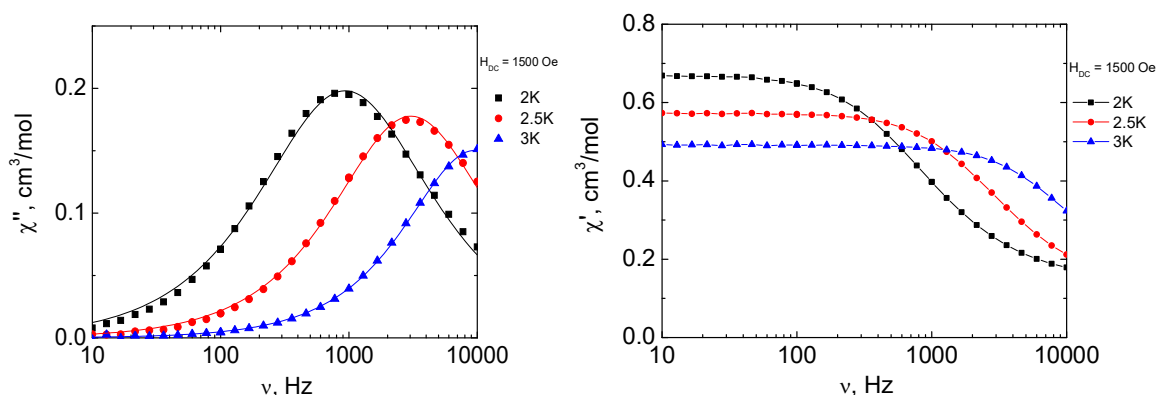
**Figure S2.** Frequency dependencies of the real,  $\chi'$  (left) and imaginary,  $\chi''$  (right) components of dynamic magnetic susceptibility for complex **4** at  $T = 2$  K under various dc magnetic fields (Oe). Solid lines are visual guides.



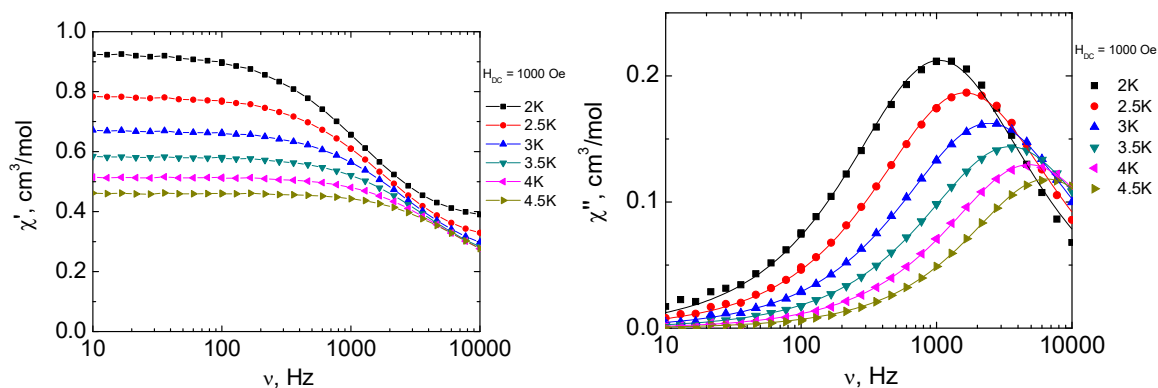
**Figure S3.** Frequency dependencies of the real,  $\chi'$  (left) and imaginary,  $\chi''$  (right) components of dynamic magnetic susceptibility for complex **5** at  $T = 2$  K under various dc magnetic fields (Oe). Solid lines are visual guides.



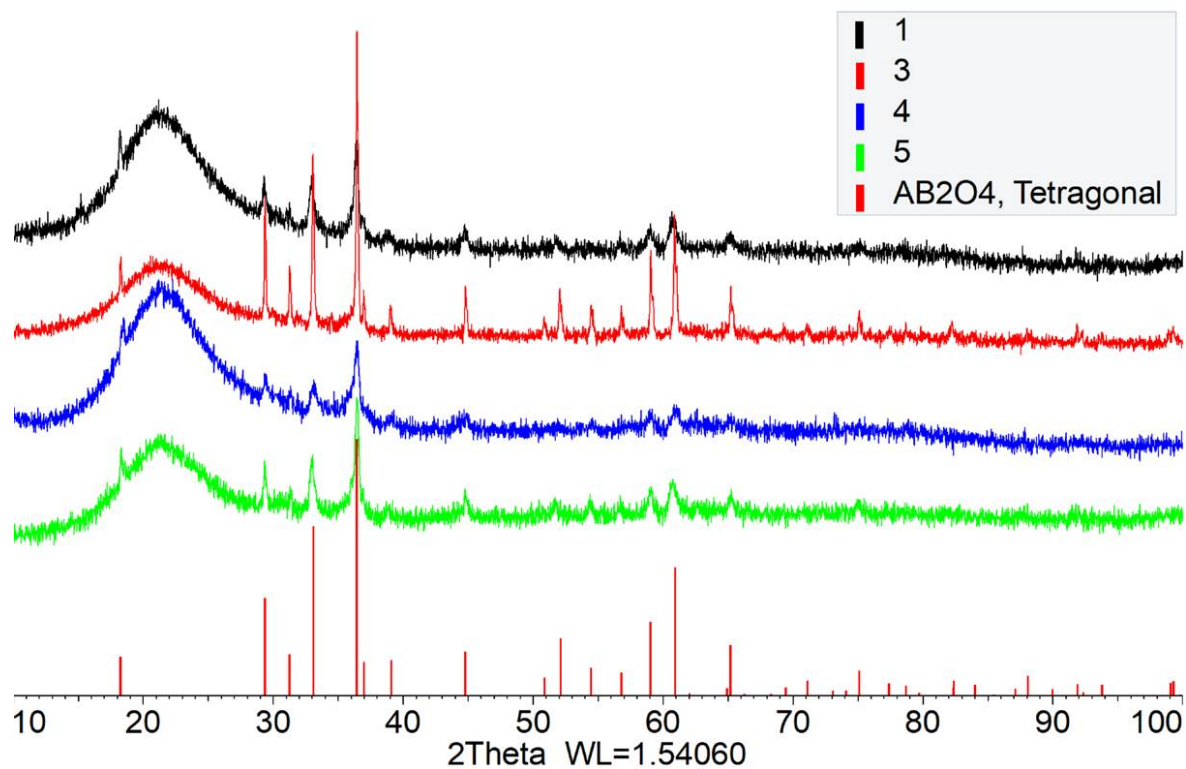
**Figure S4.** Frequency dependencies of the real ( $\chi'$ , left) and imaginary ( $\chi''$ , right) parts of the ac susceptibility for complex **1** at 2500 Oe (2-7.2 K). Lines represent visual guides (left) and approximations of the experimental data by the generalized Debye model (right).



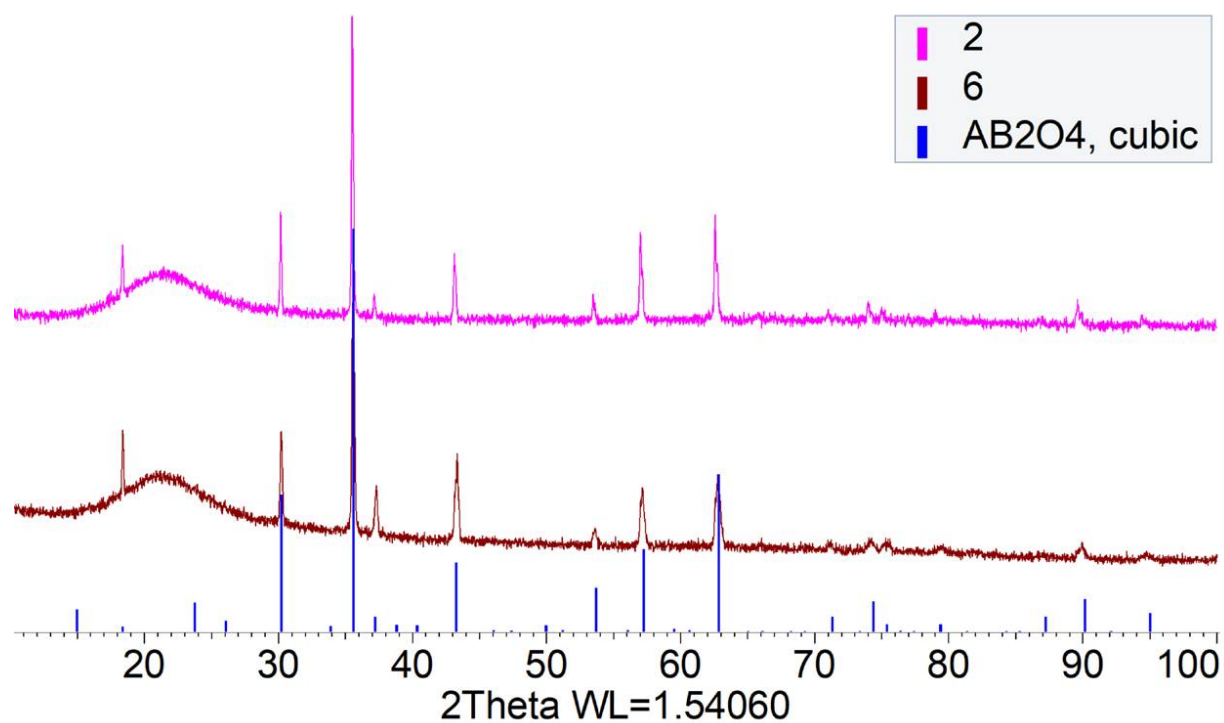
**Figure S5.** Frequency dependencies of the real ( $\chi'$ , left) and imaginary ( $\chi''$ , right) parts of the ac susceptibility for complex **4** at 1500 Oe (2-3 K). Lines represent visual guides (left) and approximations of the experimental data by the generalized Debye model (right).



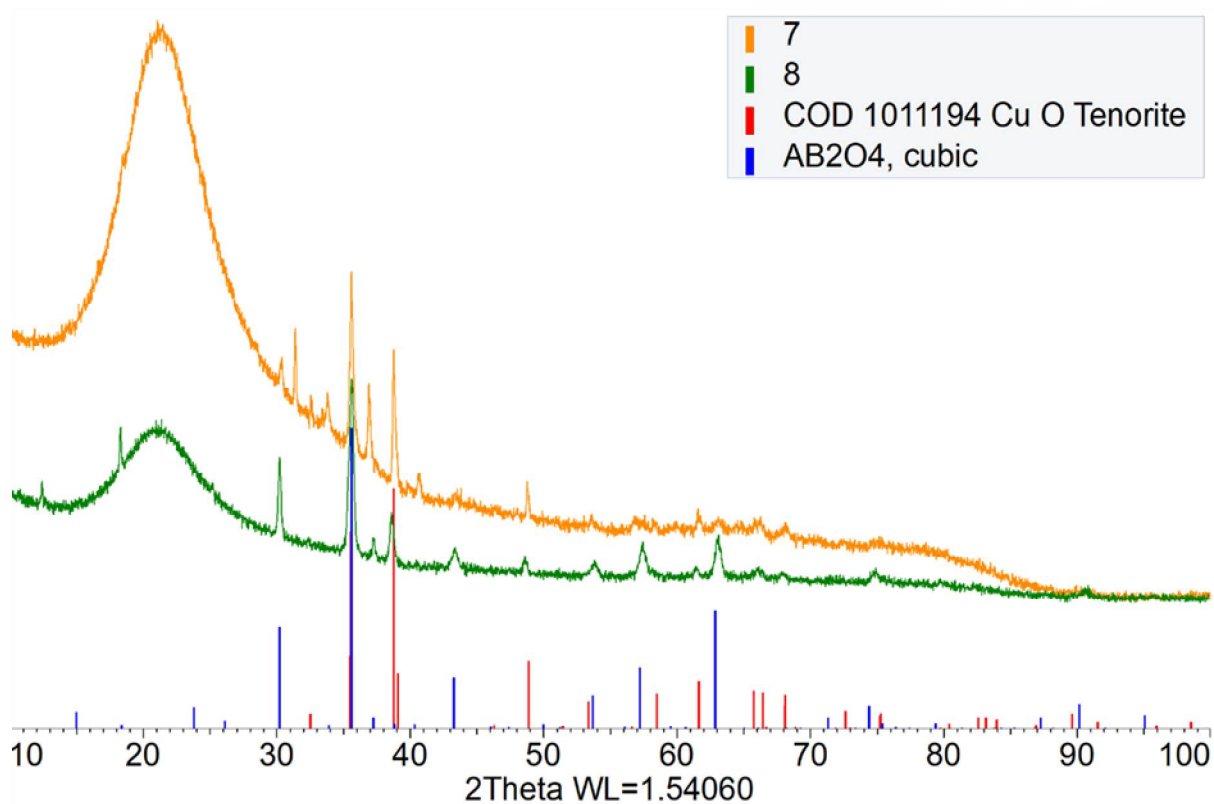
**Figure S6.** Frequency dependencies of the real ( $\chi'$ , left) and imaginary ( $\chi''$ , right) parts of the ac susceptibility for complex **5** at 1000 Oe (2-4.5 K). Lines represent visual guides (left) and approximations of the experimental data by the generalized Debye model (right).



**Figure S7.** Powder X-ray diffraction patterns of solid oxidative thermolysis products obtained from the complexes **1** (black line), **3** (red line), **4** (blue line), and **5** (green line). Vertical sticks represent the X-ray diffraction patterns of tetragonal spinel AB<sub>2</sub>O<sub>4</sub>.



**Figure S8.** Powder X-ray diffraction patterns of solid oxidative thermolysis products obtained from Ni complexes **2** (magenta line) and **6** (brown line). Vertical sticks represent the X-ray diffraction patterns of cubic spinel  $\text{AB}_2\text{O}_4$ .



**Figure S9.** Powder X-ray diffraction patterns of solid oxidative thermolysis products obtained from Cu complexes **7** (orange line) and **8** (green line). Vertical sticks represent the X-ray diffraction patterns of cubic spinel  $\text{AB}_2\text{O}_4$  and  $\text{CuO}$ .