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Magneto-Structural Variety of New 3d-4f-4(5)d Heterotrimetallic Complexes

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Electronic Supplementary Information

Infrared spectra for Type 1-Type 3 families

The most relevant characteristics of the infrared spectra for the three series of compounds **1-15** are related with the cyano and iminic stretching vibrations. For **type 1** family, for Mo derivatives (**1-5**), the large three-splitted absorption gathers stretching vibrations both from terminal (2110 cm^{-1}) and bridging cyano groups (2145 and 2170 cm^{-1}). In the case of W derivatives (**6, 7**), the two-splitted band, with sharp peaks at *ca*. 2145 and 2164 cm^{-1}, is assigned to the bridging cyano ligand, the terminal ones being identified as weak absorption located at 2100 cm^{-1}. The absorption gave by the stretching vibration of the iminic bond, υ(C=N), is located at 1630 cm^{-1}. A modified pattern of absorptions related with cyano ligands was observed in the case of **type 2** series of compounds (**8-14**): a two-splitted band with peaks centered at ca. 2140 and 2180 cm^{-1} (attributed to the cyano bridges) and a lower energy absorption centered at *ca*. 2110 cm^{-1} that is asigned to the terminal cyano groups. The absorption specific to the iminic bond is shifted toward higher energy (*ca*. 1640 cm^{-1}). The distinct topology of the heterotrimetallic chain for **15** and **16** compounds (**type 3**) gave the following values of the absorption bands attributed to the cyano ligand: 2159 and 2142 cm^{-1} for bridges and 2110 for terminal ligands. The stretching vibration of the iminic bond, υ(C=N), is found at 1632 cm^{-1}.

Table S1. Crystal data and details of the crystal determinations for compound **16**

	16
Empirical formula	$C_{49}H_{47}Cu_2Pr\ MoN_{13}O_9$
M (g mol^{-1})	1325.92
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1n$
a (Å)	12.6875(8)
b (Å)	21.6973(16)
c (Å)	20.1860(14)
β (^{o})	98.203(5)
V (Å^3)	5500.0(7)
Z	4
D_c (g cm^{-3})	1.601
μ (mm^{-1})	1.920
F(000)	2652
Refinement on	F^2
Goodness of fit	0.887
R indices [I>2σ(I)]	R_1 = 0.0771 wR_2 = 0.1613
R indices (all data)	R_1 = 0.1711 wR_2 = 0.1914

Table S2. Selected bond lengths (Å) for compounds **1**-**6 (**Ln1 = La (**1**), Ce (**2**), Eu (**3**), Tb (**4**), Ho (**5**), M1= Mo; Ln1 = Tb (**6**), M1 = W).

	1	**2**	**3**	**4**	**5**	**6**
Cu1-N1	1.971(5)	1.960(6)	1.981(5)	1.976(6)	1.954(9)	1.970(5)
Cu1-N2	1.992(5)	1.999(5)	1.980(5)	1.987(5)	1.977(9)	1.981(5)
Cu1-N7[a*]	2.311(5)	2.318(6)	2.323(5)	2.312(6)	2.340(8)	2.324(6)
Cu1-O2	1.967(4)	1.967(3)	1.959(4)	1.960(4)	1.946(6)	1.955(4)
Cu1-O3	1.998(4)	1.997(5)	1.998(4)	2.008(5)	1.991(6)	1.992(4)
Cu2-N3	1.962(6)	1.971(6)	1.974(6)	1.984(6)	1.969(9)	1.972(6)
Cu2-N4	1.975(5)	1.971(6)	1.974(5)	1.994(6)	1.961(8)	1.977(5)
Cu2-N5	2.340(5)	2.345(7)	2.339(5)	2.325(6)	2.409(8)	2.330(6)
Cu2-O6	1.956(4)	1.953(4)	1.948(6)	1.953(4)	1.924(6)	1.939(4)
Cu2-O7	1.978(4)	1.983(4)	1.983(4)	1.987(4)	1.983(6)	1.989(4)
Ln1-N8	2.593(6)	2.584(7)	2.499(5)	2.463(6)	2.427(7)	2.462(6)
Ln1-O2	2.494(4)	2.482(4)	2.407(4)	2.392(5)	2.377(5)	2.379(4)
Ln1-O3	2.478(4)	2.456(4)	2.374(3)	2.342(4)	2.328(6)	2.345(3)
Ln1-O6	2.456(4)	2.447(4)	2.377(4)	2.354(4)	2.354(5)	2.370(4)
Ln1-O7	2.480(4)	2.461(4)	2.380(4)	2.343(4)	2.341(5)	2.358(4)
Ln1-O1	2.580(4)	2.576(4)	2.512(4)	2.493(5)	2.478(6)	2.494(4)
Ln1-O8	2.631(4)	2.630(5)	2.591(5)	2.590(4)	2.572(6)	2.585(4)
Ln1-O4	2.602(5)	2.579(5)	2.508(4)	2.473(5)	2.468(6)	2.478(5)
Ln1-O5	2.603(4)	2.580(4)	2.523(4)	2.504(4)	2.494(5)	2.488(4)
M1-C39	2.143(6)	2.143(8)	2.155(5)	2.166(6)	2.155(9)	2.151(6)
M1-C40	2.161(6)	2.162(8)	2.158(6)	2.137(7)	2.160(9)	2.171(6)
M1-C41	2.160(6)	2.161(7)	2.150(5)	2.167(6)	2.185(1)	2.150(6)
M1-C42	2.155(7)	2.165(7)	2.168(5)	2.156(7)	2.187(9)	2.156(6)
M1-C43	2.161(7)	2.174(7)	2.167(7)	2.167(7)	2.177(12)	2.159(7)
M1-C44	2.155(7)	2.143(9)	2.148(7)	2.144(8)	2.149(10)	2.142(7)
M1-C45	2.158(7)	2.158(7)	2.144(7)	2.147(7)	2.153(13)	2.155(7)
M1-C46	2.172(7)	2.160(8)	2.167(7)	2.163(7)	2.164(11)	2.137(7)

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

Table S3. Selected angle lengths (°) for compounds **1**-**6** (Ln1 = La (**1**), Ce (**2**), Eu (**3**), Tb (**4**), Ho (**5**), M1 = Mo; Ln1 = Tb (**6**), M1 = W).

	1	**2**	**3**	**4**	**5**	**6**
Cu1-N7^{a}-C41^{a*}	142.7(5)	142.6(5)	138.8(5)	138.8(5)	136.9(8)	137.3(5)
N1-Cu1–N2	94.2(2)	94.7(2)	95.6(2)	95.4(3)	95.4(4)	95.7(2)
N1-Cu1-N7^{a*}	101.2(2)	101.7(3)	98.2(2)	98.1(3)	98.0(3)	97.7(3)
N2-Cu1-N7^{a*}	91.5(2)	91.6(2)	90.6(2)	90.6(2)	88.4(3)	89.6(2)
N1-Cu1-O2	92.3(2)	92.3(2)	91.9(2)	92.2(2)	94.0(3)	92.4(2)
N1-Cu1-O3	160.3(2)	159.1(2)	160.7(2)	160.5(2)	159.3(3)	161.3(2)
N2-Cu1-O2	170.7(2)	170.4(2)	169.72(19)	169.5(2)	169.1(3)	169.4(2)
N2-Cu1-O3	91.4(2)	91.1(2)	91.7(2)	91.7(2)	92.2(3)	91.8(2)
N7^{a}-Cu1-O2*	93.67(18)	93.38(19)	95.32(17)	95.53(19)	95.6(3)	96.15(18)
N7^{a}-Cu1-O3*	97.48(19)	98.2(2)	99.58(19)	100.0(2)	101.4(3)	99.5(2)
O2-Cu1-O3	80.22(16)	80.08(17)	79.03(15)	78.86(18)	77.1(2)	78.52(15)
Cu2-N5-C39	142.7(5)	143.5(6)	142.6(5)	142.8(6)	144.1(8)	142.2(5)
N3-Cu2-N4	96.2(3)	96.4(3)	97.1(3)	96.9(3)	96.9(4)	96.9(3)
N3-Cu2-N5	96.5(3)	94.4(3)	92.3(3)	91.4(3)	91.2(4)	91.1(3)
N4-Cu2-N5	92.6(2)	94.1(2)	93.4(2)	94.4(2)	90.3(3)	94.1(2)
N3-Cu2-O6	92.2(2)	92.0(2)	92.5(2)	93.1(2)	92.8(3)	92.9(2)
N3-Cu2-O7	162.3(3)	163.3(3)	162.4(3)	161.6(3)	161.6(3)	162.4(3)
N4-Cu2-O6	170.3(2)	169.9(2)	169.02(19)	168.1(2)	170.0(3)	168.6(2)
N4-Cu2-O7	92.1(2)	91.9(2)	91.9(2)	91.7(2)	93.3(3)	91.4(2)
N5-Cu2-O6	91.11(17)	90.7(2)	91.55(16)	91.72(19)	92.0(3)	91.40(18)
N5-Cu2-O7	98.7(2)	99.43(19)	102.3(2)	104.1(2)	104.0(3)	103.8(2)
O6-Cu2-O7	78.52(15)	78.58(16)	77.45(15)	76.92(16)	76.7(2)	77.61(16)
Cu1-O2-Ln1	108.64(16)	108.41(19)	108.44(16)	108.1(2)	109.5(3)	108.62(17)
Cu1-O3-Ln1	108.18(16)	108.42(19)	108.37(16)	108.34(19)	109.8(3)	108.65(16)
Cu2-O6-Ln1	110.43(16)	110.07(18)	109.85(16)	109.58(17)	110.3(2)	109.46(17)
Cu2-O7-Ln1	108.73(16)	108.48(18)	108.48(16)	108.81(17)	108.7(2)	108.16(17)
Ln1-N8^{a}-C42*	142.6(5)	142.4(6)	147.4(5)	148.9(6)	150.3(8)	148.5(5)
N8^{a}-Ln1-O2*	77.91(16)	77.90(18)	75.76(16)	74.99(18)	75.9(2)	74.87(17)
N8^{a}-Ln1-O3*	104.40(16)	103.77(17)	101.32(16)	100.02(18)	100.8(2)	99.81(17)
N8^{a}-Ln1-O1*	70.76(19)	70.48(19)	71.22(19)	71.1(2)	70.2(2)	71.5(2)
N8^{a}-Ln1-O8*	70.00(19)	69.3(2)	68.50(19)	67.8(2)	68.7(3)	67.8(2)
N8^{a}-Ln1-O6*	117.90(16)	118.32(16)	121.43(16)	122.92(18)	119.6(2)	123.05(18)
N8^{a}-Ln1-O7*	82.84(16)	81.85(18)	81.84(15)	80.78(18)	82.2(2)	80.98(17)
O2-Ln1-O3	61.83(13)	62.19(14)	63.56(13)	64.33(14)	62.9(2)	63.84(13)
O2-Ln1-O1	62.15(12)	62.44(13)	63.57(12)	63.82(14)	64.2(2)	64.30(13)
O2-Ln1-O8	121.25(13)	120.83(14)	118.94(13)	118.69(14)	116.71(18)	118.21(14)
O2-Ln1-O6	118.89(12)	119.04(14)	119.38(13)	119.12(14)	120.46(19)	119.89(13)
O2-Ln1-O7	157.18(13)	156.19(15)	153.80(13)	151.21(16)	155.6(2)	151.68(15)
O3-Ln1-O1	123.42(13)	124.23(15)	126.76(13)	127.90(15)	126.9(2)	127.86(14)
O3-Ln1-O8	80.09(13)	79.41(14)	76.83(14)	76.20(14)	74.3(2)	76.07(14)
O3-Ln1-O6	137.14(13)	137.47(16)	136.95(12)	136.80(15)	139.4(2)	136.91(14)
O3-Ln1-O7	136.18(13)	136.07(15)	135.56(14)	136.52(15)	133.2(2)	136.23(14)
O1-Ln1-O8	138.28(15)	137.26(17)	136.78(15)	135.52(17)	136.7(2)	135.88(17)
O1-Ln1-O6	68.94(14)	69.27(15)	69.09(14)	69.36(16)	68.95(19)	69.39(15)
O1-Ln1-O7	99.97(13)	98.98(14)	96.54(14)	93.86(16)	98.3(2)	94.25(15)
O8-Ln1-O6	119.47(13)	119.71(15)	121.34(13)	121.83(14)	122.46(19)	121.58(14)
O8-Ln1-O7	61.62(13)	61.67(13)	63.05(14)	63.83(14)	63.31(19)	63.68(13)
O6-Ln1-O7	60.58(12)	61.04(14)	62.26(13)	62.88(13)	62.26(18)	62.75(13)
M1-C39-N5	178.0(6)	178.6(7)	178.7(6)	178.1(6)	179.4(11)	178.1(6)
M1-C40-N6	178.4(6)	179.7(7)	177.3(6)	179.4(7)	175.4(9)	178.5(6)
M1-C41-N7	176.0(5)	175.8(6)	176.6(5)	175.9(6)	176.1(8)	176.3(5)
M1-C42-N8	176.7(6)	177.3(7)	176.0(6)	175.7(7)	175.2(9)	176.5(6)
M1-C43-N9	179.3(6)	178.7(8)	179.0(6)	178.4(9)	179.2(11)	177.5(7)
M1-C44-N10	177.2(8)	175.7(10)	177.2(10)	176.4(11)	178.3(10)	176.5(9)
M1-C45-N11	176.0(7)	177.1(7)	175.7(7)	176.3(9)	177.1(10)	176.6(8)
M1-C46-N12	178.7(7)	177.4(8)	178.3(7)	177.7(7)	179.3(11)	178.1(6)

^{*a} = *x*, -1+*y*, *z*

Table S4. Selected bond lengths (Å) for compounds **10**-**14 (**Ln1 = Dy (**10**); M1 = Mo; Ln1 = La (**11**), Gd (**12**), Tb (**13**), Dy (**14**); M1 = W).

	10	**11**	**12**	**13**	**14**
Cu1-N1	1.915(8)	1.87(2)	1.907(11)	1.914(18)	1.91(2)
Cu1-N2	1.951(8)	1.987(18)	1.944(11)	1.926(16)	1.90(2)
Cu1-N9[a*]	2.437(7)	2.465(15)	2.473(10)	2.504(14)	2.478(19)
Cu1-O2	1.913(6)	1.934(12)	1.913(7)	1.927(11)	1.868(16)
Cu1-O3	1.911(7)	1.907(14)	1.917(7)	1.887(12)	1.925(16)
Ln1-N3	2.468(7)	2.615(13)	2.504(9)	2.482(14)	2.46(2)
Ln1-O2	2.360(5)	2.476(11)	2.366(6)	2.337(11)	2.356(14)
Ln1-O3	2.305(6)	2.428(11)	2.325(7)	2.316(11)	2.287(17)
Ln1-O1	2.567(5)	2.666(10)	2.587(6)	2.590(9)	2.560(15)
Ln1-O4	2.703(5)	2.721(11)	2.695(7)	2.715(10)	2.691(16)
Ln1-O1W	2.390(5)	2.553(11)	2.411(7)	2.409(10)	2.384(13)
Ln1-O2W	2.430(7)	2.564(13)	2.460(8)	2.444(12)	2.435(18)
Ln1-O3W	2.412(6)	2.537(14)	2.458(7)	2.445(12)	2.434(15)
Ln1-O4W	2.372(5)	2.520(11)	2.411(7)	2.403(11)	2.374(14)
M1-C19	2.156(7)	2.162(16)	2.155(8)	2.187(16)	2.15(2)
M1-C20	2.177(8)	2.152(16)	2.158(10)	2.152(16)	2.17(3)
M1-C21	2.153(9)	2.179(18)	2.164(11)	2.191(17)	2.14(3)
M1-C22	2.158(9)	2.156(19)	2.129(12)	2.149(19)	1.94(4)
M1-C23	2.177(8)	2.155(17)	2.170(9)	2.157(17)	2.16(2)
M1-C24	2.162(8)	2.148(17)	2.153(8)	2.13(2)	2.14(2)
M1-C25	2.157(8)	2.125(17)	2.159(9)	2.164(18)	2.18(2)
M1-C26	2.154(8)	2.159(16)	2.147(9)	2.159(17)	2.12(2)

Table S5. Selected angle lengths (°) for compounds **10**-**14 (**Ln1 = Dy (**10**); M1 =Mo; Ln1 = La (**11**), Gd (**12**), Tb (**13**), Dy (**14**); M1 = W).

	10	**11**	**12**	**13**	**14**
Cu1-N9[a]-C25[a*]	147.0(6)	147.1(13)	147.5(8)	146.3(2)	150.4(19)
N1-Cu1-N2	86.9(4)	87.3(9)	86.5(6)	86.5(8)	86.8(11)
N9[a]-Cu1-N1[*]	93.4(3)	94.5(8)	92.8(4)	91.9(6)	91.9(8)
N9[a]-Cu1-N2[*]	99.1(3)	100.1(7)	99.5(4)	99.8(7)	98.9(9)
N9[a]-Cu1-O2[*]	88.9(3)	90.4(6)	89.1(3)	89.5(5)	89.9(8)
N9[a]-Cu1-O3[*]	95.3(3)	94.8(5)	96.3(3)	96.2(5)	96.2(7)
N1-Cu1-O2	95.4(3)	94.9(7)	95.4(4)	95.9(7)	94.9(9)
N1-Cu1-O3	171.2(3)	170.7(8)	170.8(4)	171.7(7)	171.4(8)
N2-Cu1-O2	171.5(3)	169.0(7)	171.1(4)	170.3(6)	171.0(8)
N2-Cu1-O3	93.0(3)	91.0(7)	93.1(4)	93.8(7)	94.6(9)
O2-Cu1-O3	83.5(2)	85.1(5)	83.5(3)	82.4(5)	82.4(7)
Cu1-O2-Ln1	103.9(2)	103.9(5)	104.4(3)	104.8(5)	105.6(7)
Cu1-O3-Ln1	106.0(3)	106.5(5)	105.8(3)	107.0(5)	106.3(7)
Ln1-N3-C19	170.6(6)	171.8(12)	172.9(7)	172.0(13)	173.3(17)
N3-Ln1-O2	130.0(2)	127.9(5)	130.0(3)	130.0(5)	131.8(7)
N3-Ln1-O3	134.1(2)	135.8(4)	134.7(3)	134.8(4)	133.6(6)
N3-Ln1-O1	82.5(2)	82.5(4)	82.2(3)	81.9(4)	83.0(6)
N3-Ln1-O4	76.0(2)	81.2(4)	77.3(3)	77.0(4)	76.1(6)
N3-Ln1-O1W	141.3(2)	141.5(5)	140.6(3)	141.0(4)	140.9(6)
N3-Ln1-O2W	100.0(3)	106.6(5)	99.7(3)	98.9(5)	97.5(7)
N3-Ln1-O3W	67.8(2)	67.2(4)	67.2(3)	67.7(4)	67.2(6)
N3-Ln1-O4W	71.9(2)	72.7(4)	72.5(3)	72.1(5)	72.3(6)
O2-Ln1-O3	66.1(2)	64.0(4)	65.9(2)	65.4(4)	65.1(6)
O2-Ln1-O1	61.9(2)	59.8(4)	61.4(2)	61.8(4)	63.0(5)
O2-Ln1-O4	119.30(19)	117.1(4)	119.2(2)	119.1(4)	118.5(5)
O2-Ln1-O1W	69.5(2)	68.4(5)	69.7(3)	69.6(4)	69.4(6)
O2-Ln1-O2W	130.0(2)	125.5(4)	130.2(3)	131.1(4)	130.6(6)
O2-Ln1-O3W	124.7(2)	125.6(4)	124.4(2)	123.8(4)	125.1(6)
O2-Ln1-O4W	70.2(2)	69.2(4)	70.1(2)	70.2(4)	70.3(5)
O3-Ln1-O1	128.0(2)	123.8(4)	127.2(2)	127.1(4)	128.1(5)
O3-Ln1-O4	61.6(2)	59.9(4)	61.1(2)	61.6(4)	60.9(5)
O3-Ln1-O1W	82.6(2)	82.0(5)	82.7(3)	82.4(4)	83.1(5)
O3-Ln1-O2W	77.9(2)	76.8(5)	78.8(3)	80.1(4)	79.7(6)
O3-Ln1-O3W	145.9(2)	147.4(4)	146.4(3)	146.7(4)	146.8(5)
O3-Ln1-O4W	78.3(2)	75.4(4)	77.8(3)	78.0(4)	78.4(5)
O1-Ln1-O4	150.54(16)	153.8(4)	151.1(2)	150.4(3)	150.9(5)
O1-Ln1-O1W	81.03(19)	78.9(4)	81.4(2)	81.9(3)	81.3(5)
O1-Ln1-O2W	140.2(2)	140.0(4)	140.3(3)	139.9(4)	139.6(6)
O1-Ln1-O3W	72.7(2)	74.6(4)	73.1(2)	72.4(4)	72.3(5)
O1-Ln1-O4W	83.3(2)	84.3(4)	82.7(2)	82.4(4)	82.5(5)
O4-Ln1-O1W	128.08(18)	125.7(4)	127.1(3)	127.3(4)	127.5(5)
O4-Ln1-O2W	64.64(19)	65.0(4)	64.3(2)	64.8(4)	64.3(5)
O4-Ln1-O3W	115.85(18)	116.9(4)	116.1(2)	116.8(4)	116.2(5)
O4-Ln1-O4W	71.05(19)	71.4(4)	71.8(2)	71.6(4)	72.1(5)
O1W-Ln1-O2W	72.5(2)	70.0(4)	72.2(3)	72.5(4)	73.1(6)
O1W-Ln1-O3W	73.9(2)	75.4(5)	73.8(3)	73.6(4)	73.1(6)
O1W-Ln1-O4W	139.6(2)	137.4(5)	139.5(3)	139.6(4)	139.7(5)
O2W-Ln1-O3W	71.7(2)	73.7(5)	71.4(3)	71.0(5)	70.9(6)
O2W-Ln1-O4W	135.5(2)	135.7(4)	136.0(3)	136.3(4)	136.4(6)
O3W-Ln1-O4W	135.0(2)	136.5(4)	135.1(3)	134.8(4)	134.2(5)
M1-C19-N3	175.9(6)	174.3(14)	177.4(8)	176.7(13)	178(2)
M1-C20-N4	177.7(7)	177.0(15)	178.0(9)	177.7(15)	175.4(19)
M1-C21-N5	178.7(9)	178.8(17)	178.1(12)	178.7(17)	179(2)
M1-C22-N6	177.0(8)	174.0(19)	176.5(11)	174.1(16)	172(2)
M1-C23-N7	176.6(8)	178.8(17)	176.6(11)	176.4(16)	177(2)
M1-C24-N8	176.9(8)	177.0(16)	177.1(10)	179.8(16)	175(2)
M1-C25-N9	179.0(8)	178.4(14)	177.7(10)	177.2(17)	177(2)
M1-C26-N10	179.0(8)	179.3(17)	178.6(11)	177.3(16)	178(2)

[*a] = 1-*x*, -0.5+*y*, 1-z

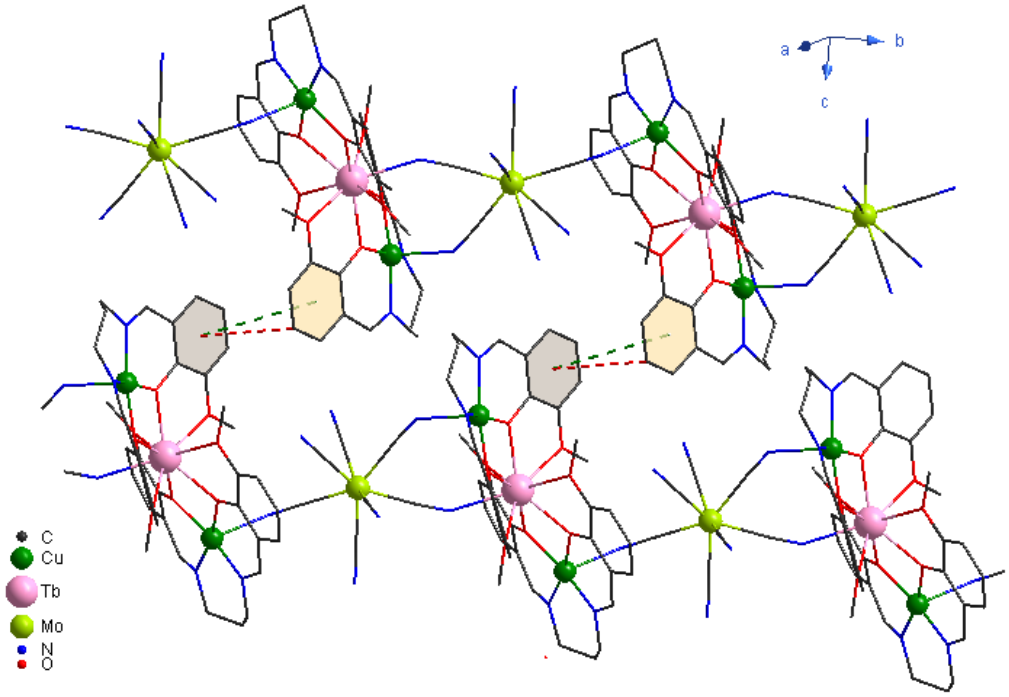


Figure S1. Fragment of the packing diagram for compound **6** showing the π-π stacking contacts between aromatic rings of two neighboring heterotrimetallic chains

Aromatic phenyl rings from Schiff base ligands belonging to adjacent chains are involved in slipped stacking interactions of C-H$\cdots\pi$ type (Figure S1). C-H group in γ position of one aromatic ring interacts with π electrons of the neighboring phenyl unit, the distance between $C_{\gamma,\ phenyl}$ and phenyl centroid being 3.62 Å. The planes of the two opposite phenyl rings are perfectly parallel (dihedral angle is 0^{o}) and the centroid-centroid distance is 4.27 Å.

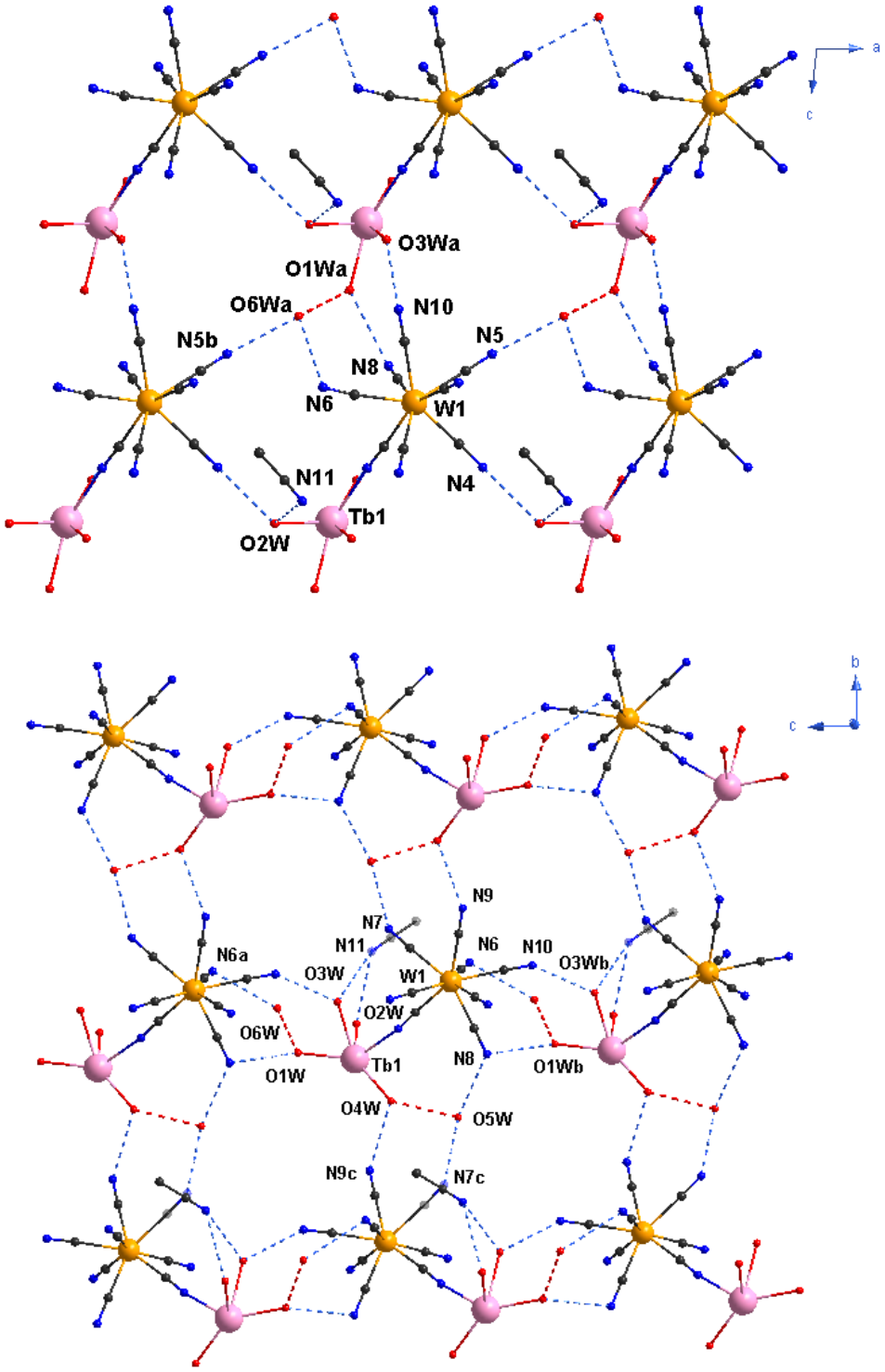


Figure S2. View in *ac* (up) and *bc* (down) plane of the packing diagram for compound **13,** showing details of the complex pattern of the N···O (blue dotted lines) and O···O (red dotted lines) type hydrogen bonds formed between free cyano ligands, coordinated and cristallization water molecules (the C and N atoms of the side-off compartmental ligand as well as the copper ions were omitted for the sake of clarity).

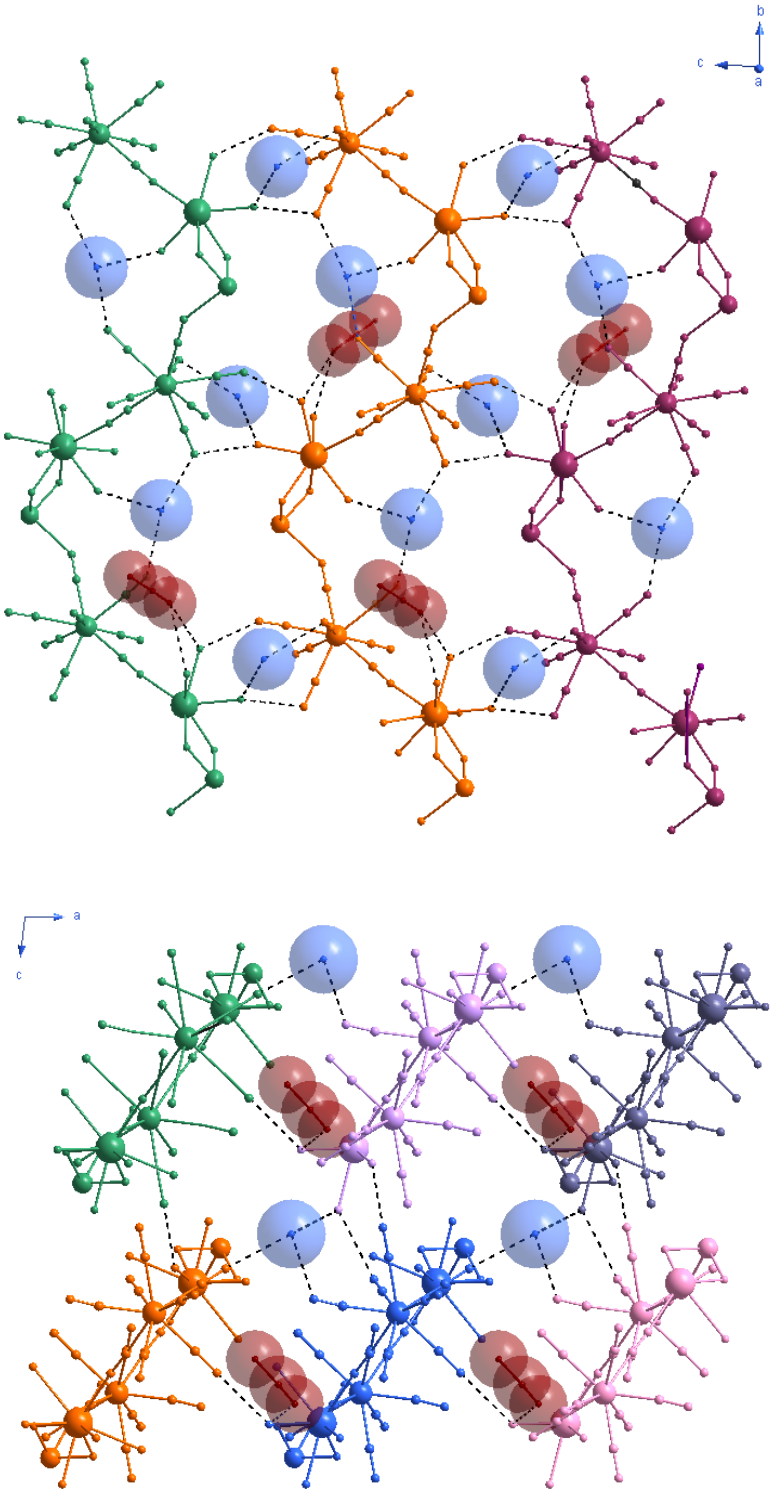


Figure S3. View in *bc* (up) and *ac* (down) plane of the packing diagram for compound **13**, showing details of the inter-connection of the neighboring chains (the C and N atoms of the side-off compartmental ligand as well as the copper ions were omitted for the sake of clarity, the water (light blue)/acetonitrile (dark red) crystallization molecules are represented as space-filling).

Table S6. Selected hydrogen-bonds distances (Å) in **10**-**14**

	10	**11**	**12**	**13**	**14**
O(1W)^{b}···N(8)*	2.936(9)	2.927(2)	2.945(2)	2.949(2)	2.962 (2)
O(2W)···N(4)	2.868(1)	2.901(2)	2.862(1)	2.862(2)	2.873(2)
O(2W)^{c}···N(11)*	3.192(1)	3.412(3)	3.096(2)	3.095(3)	3.114(4)
O(3W)^{b}···N(10)*	2.725(1)	2.700(2)	2.706(1)	2.707(2)	2.730(2)
O(3W) ···N(11)	2.876(1)	2.827(3)	2.913(2)	2.912(3)	2.906(4)
O(5W)···N(7)	2.939(1)	2.948(2)	2.964 (2)	2.966(2)	2.977(3)
O(5W)···N(8)	2.950 (1)	2.945(2)	2.992(2)	2.990(2)	2.953(3)
O(6W)···N(5)^{b*}	2.82(1)	2.824(3)	2.816(2)	2.816(2)	2.835(3)
O(6W)···N(6)	3.05(1)	2.963(3)	3.005(2)	3.004(2)	3.062 (3)
O(1W)···O(6W)	2.67(1)	2.653(3)	2.697(1)	2.697(2)	2.674(3)
O(4W)···O(5W)	2.722 (8)	2.734(2)	2.757(1)	2.756(2)	2.771(2)

$^{*\,b}$ = *x*, *y*, -1+*z*; ^{c} = 1-*x*, -1/2+*y*, 1-*z*

The analysis of the packing diagram for compound **13** reveals the formation of a three-dimensional supramolecular network constructed by intra- and intermolecular hydrogen bonds established between terminal cyano ligands and water molecules (crystallization and coordination molecules). All terminal cyano ligands of the $[M^{V}(CN)_8]^{3-}$ anion act as H-acceptors for oxygen atoms belonging to crystallization water molecules (O5W and O6W) and aqua ligands (O1W-O4W). The crystallization solvent molecules (water and acetonitrile molecules) are intramolecular bound to the heterotrimetallic chains through O1W···O6W, N7^{c}···O5W and O3W···N11 hydrogen bonds. Supramolecular layers are developed, in *ac* plane, by neighbouring chains, connected through hydrogen bonds and employ one octacyanometallate(V) unit from one chain and $\{Ln^{III}(H_2O)_4\}$ moiety from an adjacent chain (Figure S2 top and S3 bottom). Adjacent layers are further linked, in *bc* plane, through the N7^{c}···O5W···N8 and O4W···N9^{c} non-covalent "bridges" (Figure S2 bottom and S3 top) building a supramolecular three-dimensional framework.

Table S7. Selected bond (Å) and angle (°) legths for compound **15.**

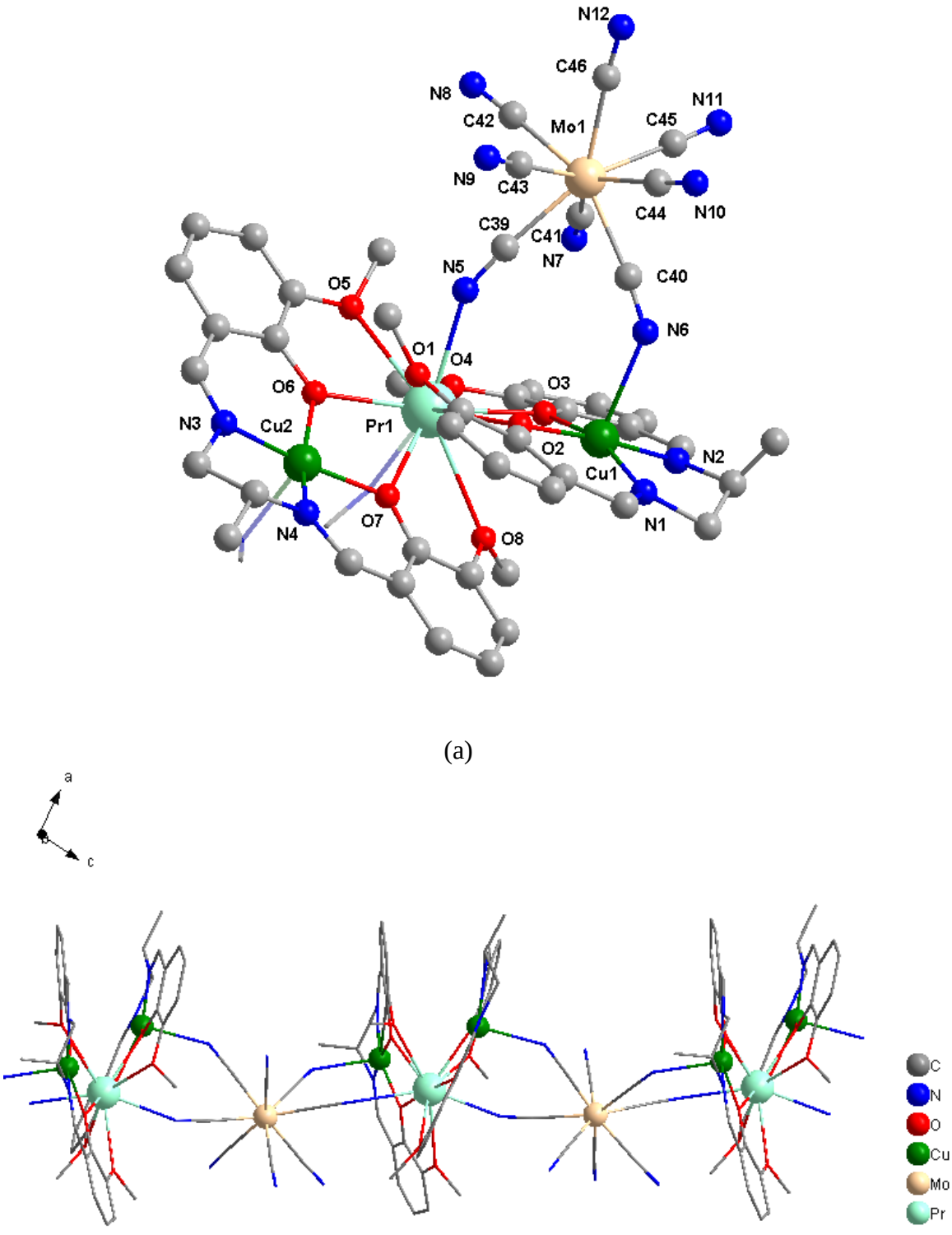
	15		
Cu1-N1	1.926(10)	N3-La1-O2^{a*}	81.77(2)
Cu1-N2	1.947(10)	N3-La1-O2	95.9(2)
Cu1^{a}-N6*	2.485(1)	N3-La1-O3^{a*}	72.1(2)
Cu1-O2	1.944(5)	N3-La1-O3	130.8(2)
Cu1-O3	1.918(6)	N3-La1-O1^{a*}	91.4(2)
La1-N3	2.651(7)	N3-La1-O1	65.5(2)
La1-O2	2.489(4)	N3-La1-O4^{a*}	65.7(3)
La1-O3	2.448(6)	N3-La1-O4	134.7(2)
La1-O1	2.797(6)	O2-La1-O2^{a*}	170.3(3)
La1-O4	2.796(7)	O2-La1-O3	63.66(2)
Mo1-C20	2.156(7)	O2a-La1-O3^{a*}	124.7(2)
Mo1-C21	2.143(10)	O2-La1-O1^{a*}	112.9(2)
Mo1-C23	2.177(9)	O2-La1-O1	57.94(2)
Mo1-C24	2.169(9)	O2-La1-O4^{a*}	66.6(2)
Cu1^{a}-N6-C24	132.3(3)	O2-La1-O4	120.1(2)
N1-Cu1-N2	85.5(5)	O3-La1-O3^{a*}	83.7(3)
N6-Cu1^{a}-N1^{a*}	88.3(3)	O3-La1-O1^{a*}	137.36(2)
N6-Cu1^{a}-N2^{a*}	98.3(2)	O3-La1-O1	120.97(2)
N6-Cu1^{a}-O2^{a*}	98.0(2)	O3-La1-O4^{a*}	65.1(2)
N6-Cu1^{a}-O3^{a*}	98.6(3)	O3-La1-O4	59.2(2)
O2-Cu1-O3	84.7(2)	O1-La1-O1^{a*}	65.8(3)
O2-Cu1-N1	93.8(3)	O1-La1-O4	156.4(3)
O2-Cu1-N2	163.7(3)	O1-La1-O4^{a}	97.8(3)
O3-Cu1-N1	173.1(4)	O4-La1-O4^{a}	102.5(4)
O3-Cu1-N2	94.0(4)	Mo1-C20-N3	175.3(8)
Cu1-O2-La1	104.2(2)	Mo1-C21-N4	176.7(10)
Cu1-O3-La1	106.6(2)	Mo1-C23-N5	179.1(11)
La1-N3-C20	153.2(7)	Mo1-C24-N6	174.7(8)

^{*a} = *x, -y, -z*

Table S8. Selected bond (Å) and angle (°) lengths for compound **16**

	16		
Cu1-N1	1.894(12)	Pr1-N5-C39	153.1(8)
Cu1-N2	1.956(11)	Pr1-N12^{a}-C46^{a*}	154.0(9)
Cu1-N6	2.368(10)	N5-Pr1-O2	75.9(3)
Cu1-O2	1.933(7)	N5-Pr1-O3	82.0(3)
Cu1-O3	1.936(8)	N5-Pr1-O6	93.6(3)
Cu2-N3	1.924(11)	N5-Pr1-O7	128.4(3)
Cu2-N4	1.874(15)	N5-Pr1-O1	64.6(3)
Cu2-N10	2.346(11)	N5-Pr1-O4	91.8(3)
Cu2-O6	1.947(8)	N5-Pr1-O5	64.2(3)
Cu2-O7	1.927(7)	N5-Pr1-O8	139.0(3)
Pr1-N5	2.560(8)	N12^{a}-Pr1-O2*	133.3(3)
Pr1-N12^{a*}	2.607(10)	N12^{a}-Pr1-O3*	100.1(3)
Pr1-O2	2.454(7)	N12^{a}-Pr1-O6*	80.8(3)
Pr1-O3	2.472(7)	N12^{a}-Pr1-O7*	77.1(3)
Pr1-O6	2.450(7)	N12^{a}-Pr1-O1*	136.2(3)
Pr1-O7	2.414(7)	N12^{a}-Pr1-O4*	64.0(3)
Pr1-O1	2.903(8)	N12^{a}-Pr1-O5*	86.9(3)
Pr1-O4	2.755(9)	N12^{a}-Pr1-O8*	66.5(3)
Pr1-O5	2.786(8)	N5-Pr1-N12^{a*}	148.7(3)
Pr1-O8	2.790(7)	O2-Pr1-O3	64.3(3)
Mo1-C39	2.133(9)	O2-Pr1-O1	56.5(2)
Mo1-C40	2.158(13)	O2-Pr1-O4	123.4(2)
Mo1-C41	2.156(15)	O2-Pr1-O5	139.7(2)
Mo1-C42	2.169(14)	O2-Pr1-O8	67.0(2)
Mo1-C43	2.202(13)	O3-Pr1-O1	116.7(2)
Mo1-C44	2.159(12)	O3-Pr1-O4	59.3(3)
Mo1-C45	2.143(12)	O3-Pr1-O5	113.6(2)
Mo1-C46	2.172(11)	O3-Pr1-O8	66.9(2)
Cu1-N6-C40	136.4(9)	O1-Pr1-O4	156.2(2)
N6-Cu1-N1	100.7(5)	O1-Pr1-O5	98.4(2)
N6-Cu1-N2	91.2(4)	O1-Pr1-O8	105.6(2)
N6-Cu1-O2	94.6(3)	O4-Pr1-O5	66.3(2)
N6-Cu1-O3	98.5(4)	O4-Pr1-O8	94.2(2)
N1-Cu1-N2	84.6(6)	O5-Pr1-O8	152.5(2)
N1-Cu1-O2	94.9(4)	Mo1-C39-N5	173.0(9)
N1-Cu1-O3	160.7(4)	Mo1-C40-N6	173.8(10)
N2-Cu1-O2	174.2(4)	Mo1-C41-N7	176.0(12)
N2-Cu1-O3	93.2(5)	Mo1-C42-N8	176.8(11)
Cu2-N10^{a}-C44^{a*}	138.0(9)	Mo1-C43-N9	178.6(11)
N10^{a}-Cu2-N3*	94.4(4)	Mo1-C44-N10	177.4(10)
N10^{a}-Cu2-N4*	97.9(4)	Mo1-C45-N11	176.4(11)
N10^{a}-Cu2-O6*	99.4(4)	Mo1-C46-N12	173.7(10)
N10^{a}-Cu2-O7*	92.7(3)		
N3-Cu2-N4	84.7(6)		
N3-Cu2-O6	94.6(5)		
N3-Cu2-O7	172.9(4)		
N4-Cu2-O6	162.8(4)		
N4-Cu2-O7	93.7(4)		
Cu1-O2-Pr1	104.9(3)		
Cu1-O3-Pr1	104.2(3)		
Cu2-O6-Pr1	103.5(3)		
Cu2-O7-Pr1	105.4(3)		

^{*a} = ½+*x*, ½-*y*, ½+*z*



(a)

(b)

Figure S4. (a) The heterotrimetallic unit in **16** with the atom numbering. (b) View of a fragment of the 1-D coordination polymer of **16.**

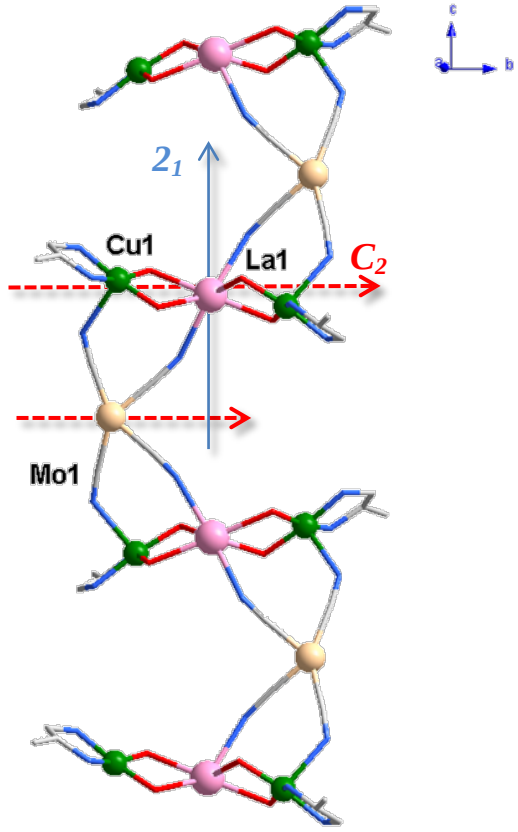


Figure S5. Fragment of the helicoidal motif in **15.** Free cyano groups of $[Mo(CN)_8]^{3-}$ anion and the side-off ligands, excepting phenoxo bridges and 1,2-propanediamine arms, were omitted for the sake of clarity. The screw axis 2_1 and the two-fold axis, C_2, crossing the asymmetric unit are represented as blue and red-dotted arrows.

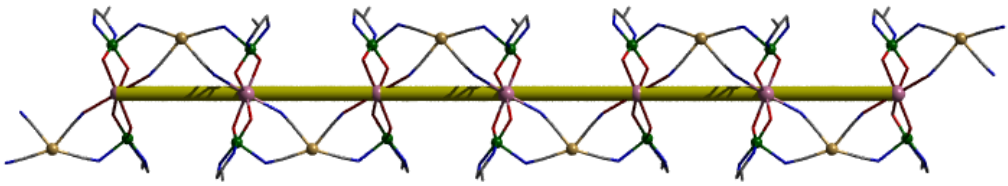


Figura S6. View of a fragment of the 1-D structure for compound **15** that shows the enfolding of the heterometallic chain around the 2_1 screw axis (the carbon atom of the phenyl rings of the compartmental ligand as well as free cyano groups were omitted for the sake of clarity).

In compound **15**, one 2_1 screw axis is parallel to the *c* axis and passes through the lanthanum(III) ion, the chain being enfolded around this axis in a left-handed helicoidal arrangement (Figure S6).

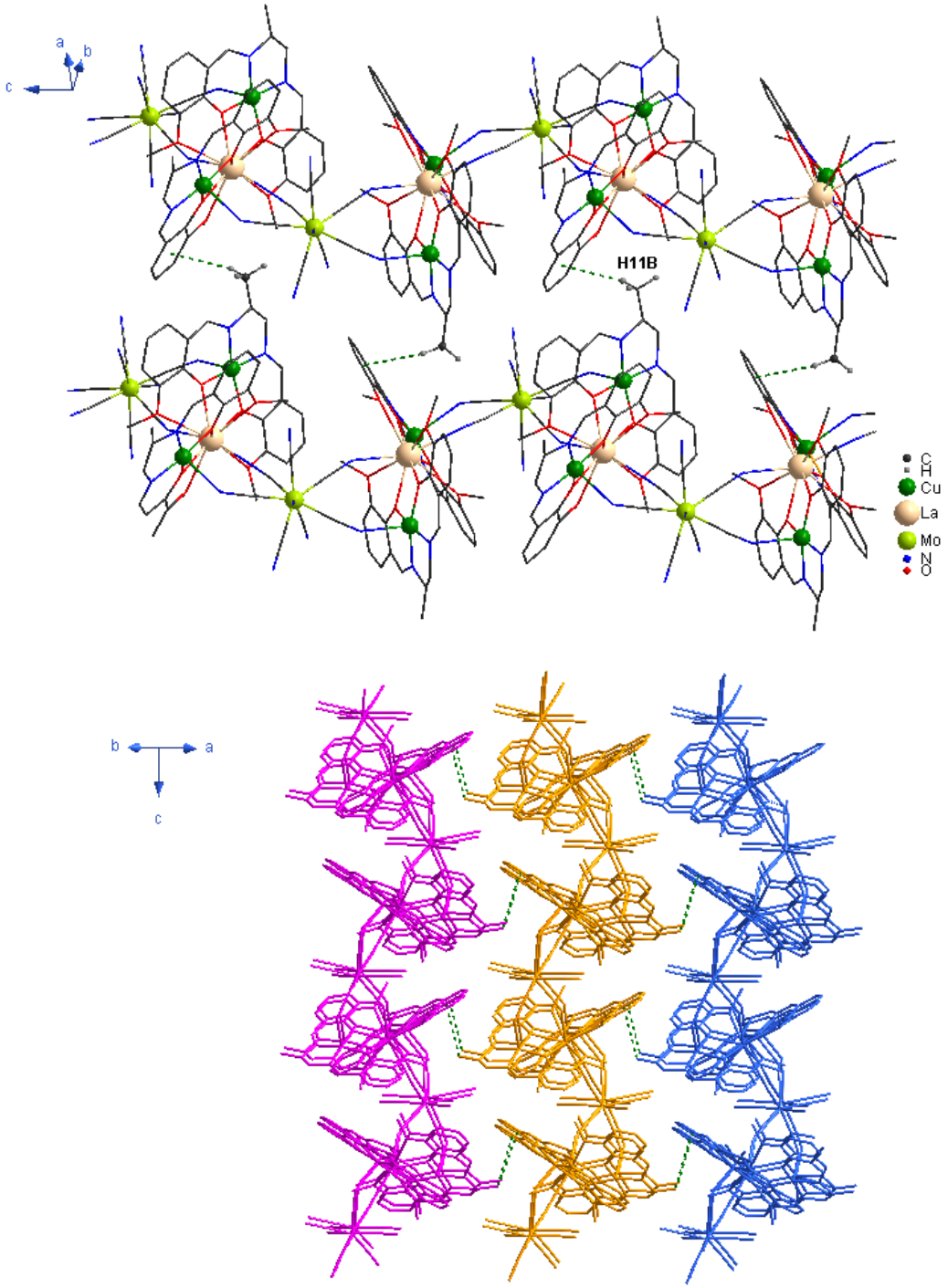


Figure S7. View of the crystal packing for compound **15**: (up) supramolecular layers resulted from the C-H$\cdots\pi$ interactions; (bottom) the extended supramolecular three-dimensional network formed between adjacent layers (represented in magenta, yellow and blue color) through C-H$\cdots\pi$ interactions. The distance between the H11 atom and the centroid of the phenyl ring is 2.77 Å.

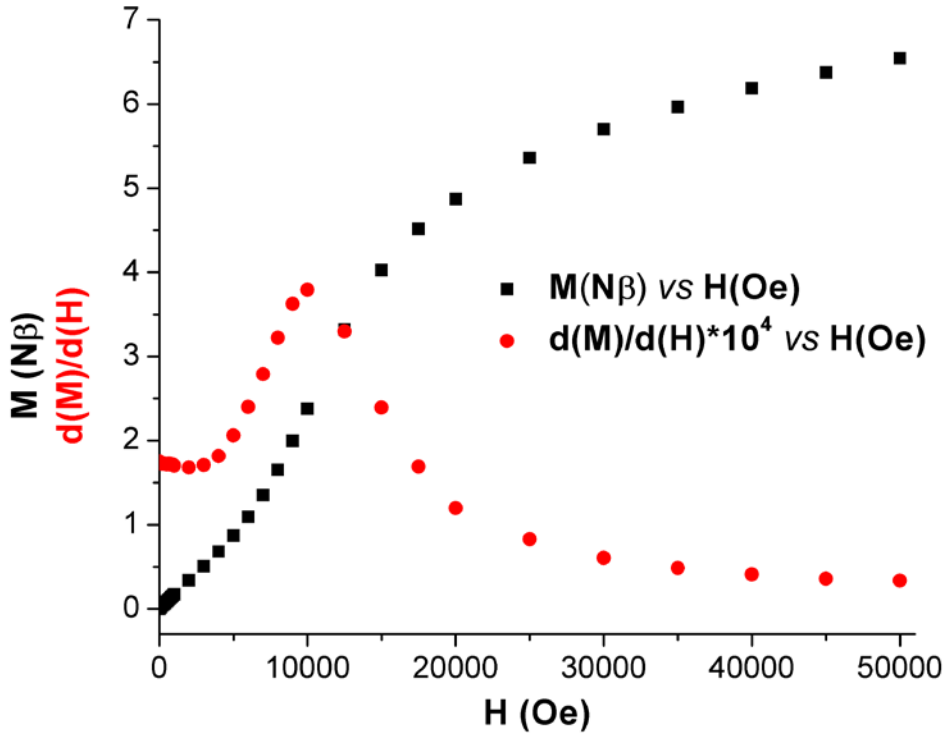


Figure S8. Field dependence of the magnetization at 2 K and d*M*/d*H* derivative for **4**

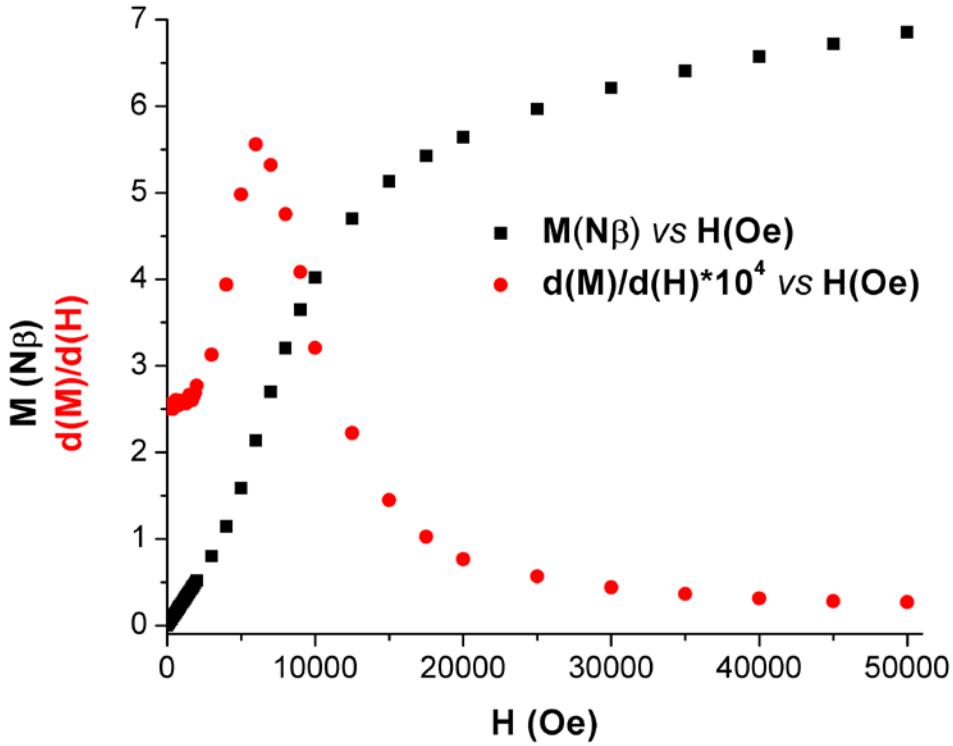


Figure S9. Field dependence of the magnetization at 2 K and d*M*/d*H* derivative for **6**.

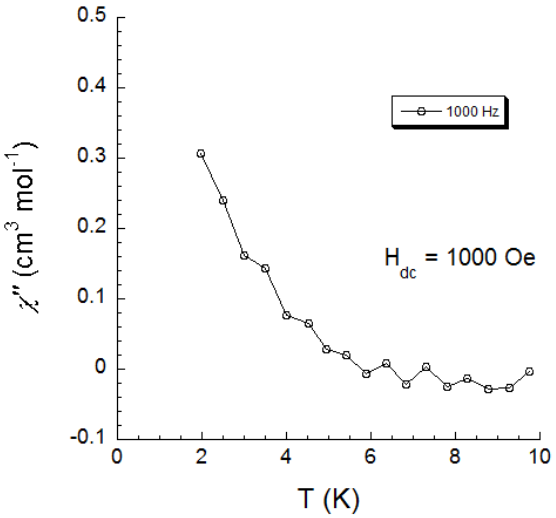


Figure S10. Temperature dependence of the out-of-phase component (χ_M'') of **9**, under an applied field of 1000 Oe with an ac field of 3 Oe with a frequency of 1000 Hz. Solid line is an eye-guide.

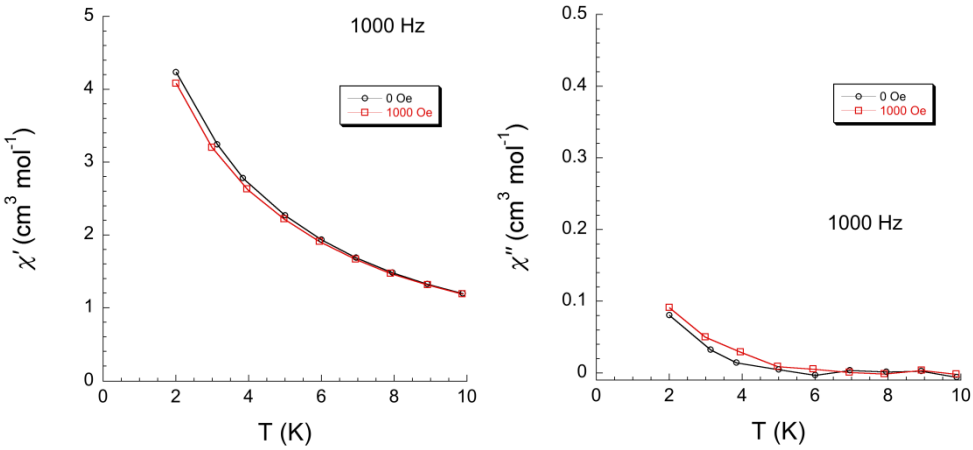


Figure S11. χ_M' (left) and χ_M'' (right) components of compound **13** between 2 and 10 K under zero DC field or under an applied DC field of 1000 Oe with an ac field of 3 Oe with a frequency of 1000 Hz. Solid lines are eye-guides.

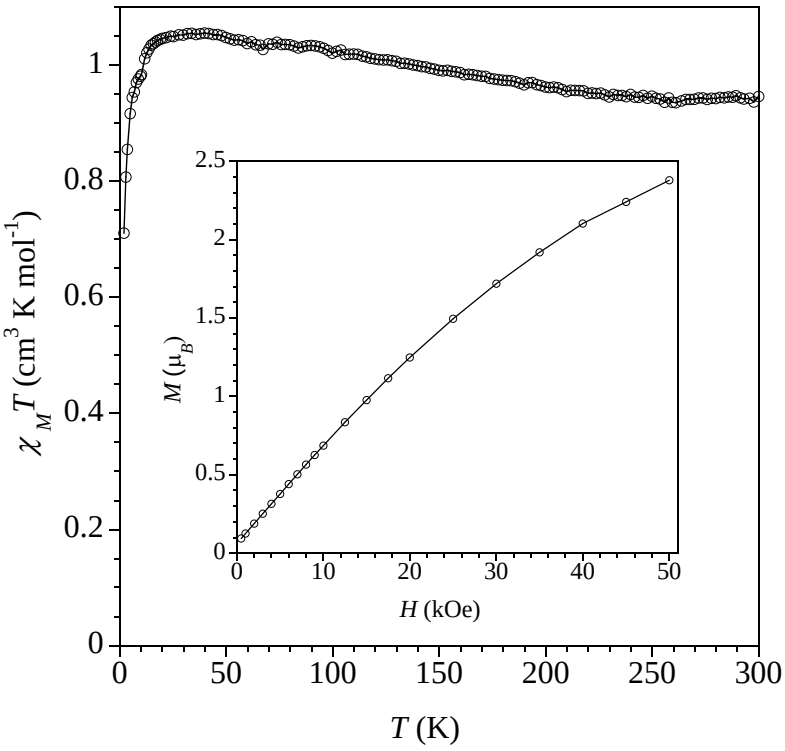


Figure S12. Temperature dependence of the $\chi_M T$ product per mole of **15** at 1000 Oe. Inset: the field dependence of the magnetization for compounds **15**. The solid line is an eye-guide.