Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

Metallomacrocycle or coordination polymer: Spacer-directed self-assembly of transition-metal complexes based on flexible bis(benzotriazole) ligands

Xiao-Liang Tang, Wei Dou, Ji-an Zhou, Guo-Lin Zhang, Wei-Sheng Liu,* Li-Zi Yang and Yong-Liang Shao

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China.

* Corresponding author：E-mail: liuws@lzu.edu.cn

Fax: +86-931-8912582; Tel: +86-931-8915151;

Contents

Table S1 Selected bond lengths (Å), angles (°) and weak interaction for complex **1**

Ag(1)-O(1)	2.578(3)	Ag(1)-N(8)	2.553(4)
Ag(1)-N(1)	2.247(3)	Ag(1)-N(4)^{i}	2.213(3)
O(1)-Ag(1)-N(1)	81.42(10)	N(1)-Ag(1)-N(8)	91.61(14)
O(1)-Ag(1)-N(8)	136.75(18)	N(1)-Ag(1)-N(4)^{i}	151.17(11)
O(1)-Ag(1)-N(4)^{i}	107.84(10)	N(8)-Ag(1)-N(4)^{i}	98.65(15)
N(3)-C(7)-C(8)-N(6)		-61.6(4)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(8)–H(8A)···O(1)^{ii}	0.97	2.38	3.307(5)	160
C(8)–H(8B)···O(3)^{iii}	0.97	2.37	3.292(5)	158
C(15)–H(15C)···N(5)^{iv}	0.96	2.61	3.353(6)	134

π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(1)^{v}	0	3.5396(17)
Cg(1)–Cg(2)^{v}	0.99	3.6840(19)

Symmetry codes: i) x, -1+y, z; ii) 2-x, 2-y, 2-z; iii) 1+x, 1+y, z; iv) 2-x, 2-y, 1-z; v) 2-x, 3-y, 2-z; Ring Cg(1): N(4)–N(5)–N(6)–C(14)–C(9); Ring Cg(2): C(9)–C(10)–C(11)–C(12)–C(13)–C(14).

Table S2 Selected bond lengths (Å), angles (°) and weak interaction for complex **2**

Ag(1)-N(1)	2.243(5)	Ag(1)-N(1)^{ii}	2.243(9)
Ag(1)-N(1)^{i}	2.243(8)	Ag(1)-Ag(1)^{iii}	3.186(1)
N(1)-Ag(1)-N(1)^{i}	120.0(3)	N(1)-Ag(1)-Ag(1)^{iii}	88.95(13)
N(1)-Ag(1)-N(1)^{ii}	120.0(2)	N(1)^{i}-Ag(1)-Ag(1)^{iii}	88.95(13)
N(1)^{i}-Ag(1)-N(4)^{ii}	120.0(3)	N(1)^{ii}- Ag(1)-Ag(1)^{iii}	88.95(13)
N(3)-C(7)-C(8)-O(1)		-68.1(1)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(3)–H(3)···N(2)^{i}	0.93	2.59	3.491(11)	163
C(6)–H(6)···O(2)^{iv}	0.93	2.36	3.219(10)	153
C(7)–H(7A)···O(2)^{v}	0.97	2.57	3.214(9)	124
C(8)–H(8B)···O(2)^{v}	0.97	2.45	2.947(13)	111

π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(2)^{vi}	10.23	3.968(4)
Cg(2)–Cg(2)^{vi}	11.20	3.663(4)

Symmetry codes: i) 1-y, 1+x-y, z; ii) -x+y, 1-x, z; iii) -1/3+y, 1/3+x, 5/6-z; iv) 1+x-y, 1+x, 1-z; v) 1-x, 2-y, 1-z; vi) 2/3-x, 1/3-x+y, 5/6-z; Ring Cg(1): N(1)–N(2)–N(3)–C(1)–C(2); Cg(2): C(1)–C(2)–C(3)–C(4)–C(5)–C(6).

Table S3 Selected bond lengths (Å), angles (°) and weak interaction for complex **3**

Ag(1)-O(3)	2.424(2)	Ag(1)-O(3)^{i}	2.590(2)
Ag(1)-N(1)	2.199(2)	Ag(1)-N(6)^{ii}	2.217(2)
O(3)-Ag(1)-N(1)	112.18(7)	N(1)-Ag(1)-O(3)^{i}	105.78(7)
O(3)-Ag(1)-O(3)^{i}	75.99(7)	N(1)-Ag(1)-N(6)^{ii}	134.41(7)
O(3)-Ag(1)-N(6)^{ii}	109.14(7)	O(3)^{i} -Ag(1)-N(6)^{ii}	102.05(7)
Ag(1)-O(3)-Ag(1)^{i}	104.01(7)		
N(3)-C(7)-C(8)-O(1)		-67.5(3)	
O(2)-C(11)-C(12)-N(4)		-62.8(3)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(8)–H(8B)···O(2)	0.97	2.36	3.016(3)	125
C(12)–H(12B)···O(3)^{iii}	0.97	2.54	3.447(3)	156
C(14)–H(14)···O(5)^{iii}	0.93	2.57	3.499(4)	176

π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(1)^{iv}	0	3.5487(18)
Cg(1)–Cg(2)^{iv}	0.96	3.7593(19)
Cg(2)–Cg(3)^{v}	25.87	3.991(2)

Symmetry codes: i) -1-x, 2-y, 2-z; ii) -x, 2-y, 2-z; iii) -x, 1-y, 2-z; iv) 1-x, 1-y ,2-z; v) -x, -1/2+y, 3/2-z; Ring Cg(1): N(4)–N(5)–N(6)–C(18)–C(13); Cg(2): C(13)–C(14)–C(15)–C(16)–C(17)–C(18); Cg(3): C(1)–C(2)–C(3)–C(4)–C(5)–C(6).

Table S4 Selected bond lengths (Å), angles (°) and weak interaction for complex **4**

Cu(1)-Cl(1)	2.2311(13)	Cu(1)-N(1)	1.987(3)
Cu(1)-Cl(2)	2.2064(16)	Cu(1)-N(4)^{i}	1.985(3)
Cl(1)-Cu(1)-Cl(2)	156.24(6)	Cl(2)-Cu(1)-N(1)	90.85(10)
Cl(1)-Cu(1)-N(1)	92.90(10)	Cl(2)-Cu(1)-N(4)^{i}	91.96(10)
Cl(1)-Cu(1)-N(4)^{i}	93.18(9)	N(1)-Cu(1)-N(4)^{i}	158.19(13)
N(3)-C(7)-C(8)-N(6)		63.5(4)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(7)–H(7B)···Cl(1)^{ii}	0.97	2.75	3.716(4)	173
C(8)–H(8A)···N(5)^{iii}	0.97	2.45	3.347(5)	153

π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(1)^{ii}	0.03	3.681(2)
Cg(1)–Cg(2)^{ii}	3.81	3.916(2)
Cg(2)–Cg(3)^{iv}	26.66	3.798(3)
Cg(3)–Cg(3)^{v}	0	3.865(3)

Symmetry codes: i) x, 1+y, z; ii) -x, 2-y, -z; iii) 1-x, 1-y, -z; iv) x, y , z; v) 1-x, 1-y, 1-z; Ring Cg(1): N(1)–N(2)–N(3)–C(6)–C(1); Ring Cg(2): C(1)–C(2)–C(3)–C(4)–C(5)–C(6); Ring Cg(3): C(9)–C(10)–C(11)–C(12)–C(13)–C(14).

Table S5 Selected bond lengths (Å), angles (°) and weak interaction for complex **5**

Cu(1)-Cl(1)	2.5334(8)	Cu(1)-N(1)	2.007(2)
Cu(1)-Cl(2)	2.2749(9)	Cu(1)-N(4)^{i}	2.006(2)
Cu(1)-Cl(1)^{i}	2.3782(8)		
Cl(1)-Cu(1)-Cl(2)	117.20(3)	Cl(1)-Cu(1)-N(4)^{i}	93.97(7)
Cl(1)-Cu(1)-N(1)	93.57(7)	Cl(1)^{i}-Cu(1)-Cl(2)	152.58(3)
Cl(1)-Cu(1)-Cl(1)^{i}	90.19(3)	Cl(2)-Cu(1)-N(4)^{i}	89.13(7)
Cl(2)-Cu(1)-N(1)	88.80(7)	N(1)-Cu(1)-N(4)^{i}	172.30(10)
Cl(1)^{i}-Cu(1)-N(1)	90.73(7)	Cu(1)	89.81(3)
Cl(1)^{i}-Cu(1)-N(4)^{i}	87.70(7)	-Cl(1)-Cu(1)^{i}	
N(3)-C(7)-C(8)-O(1)		67.4(3)	
O(1)-C(9)-C(10)-N(6)		-62.0(3)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(7)–H(7B)···O(1)^{ii}	0.97	2.57	3.524(4)	166
C(10)–H(10B)···N(5)^{iii}	0.97	2.50	3.423(4)	159
C(14)–H(14)···Cl(1)^{iv}	0.93	2.79	3.676(4)	160
C(15)–H(15)···Cl(1)^{i}	0.93	2.78	3.407(3)	126

π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(2)^{v}	14.12	3.9141(15)
Cg(1)–Cg(3)^{v}	13.33	3.8316(17)
Cg(2)–Cg(3)^{vi}	0.84	3.6717(16)
Cg(4)–Cg(4)^{vii}	0.03	3.8546(18)
Cg(3)–Cg(4)^{v}	13.79	3.8375(17)
Cg(3)–Cg(3)^{vi}	0	3.7242(17)

Symmetry codes: i) 2-x, -y, -z; ii) 1-x, 1-y, 1-z; iii) 2-x, 1-y, -z; iv) -1+x, y, z; v) x, y, z; vi) 1-x, 1-y, -z; vii) 1-x, -y, 1-z; Ring Cg(1): N(1)–N(2)–N(3)–C(6)–C(1); Cg(2): N(4)–N(5)–N(6)–C(11)–C(16); Cg(3): C(11)–C(12)–C(13)–C(14)–C(15)–C(16); Cg(4): C(1)–C(2)–C(3)–C(4)–C(5)–C(6).

Table S6 Selected bond lengths (Å), angles (°) and weak interaction for complex **6**

Cu(1)-Cl(1)	2.286(3)	Cu(2)-Cl(3)	2.245(3)
Cu(1)-Cl(2)	2.4370(19)	Cu(2)-Cl(4)	2.2937(19)
Cu(1)-O(5)	2.090(7)	Cu(2)-O(6)	2.340(6)
Cu(1)-N(1)	1.999(5)	Cu(2)-N(6)	2.035(6)
Cu(1)-N(12)	1.997(6)	Cu(2)-N(7)	2.045(6)
Cl(1)-Cu(1)-Cl(2)	120.12(10)	Cl(3)-Cu(2)-Cl(4)	148.29(11)
Cl(1)-Cu(1)-O(5)	144.2(2)	Cl(3)-Cu(2)-O(6)	103.03(16)
Cl(1)-Cu(1)-N(1)	89.7(2)	Cl(3)-Cu(2)-N(6)	91.71(19)
Cl(1)-Cu(1)-N(12)	88.8(2)	Cl(3)-Cu(2)-N(7)	92.5(2)
Cl(2)-Cu(1)-O(5)	95.7(2)	Cl(4)-Cu(2)-O(6)	108.66(16)
Cl(2)-Cu(1)-N(1)	93.0(2)	Cl(4)-Cu(2)-N(6)	90.00(19)
Cl(2)-Cu(1)-N(12)	90.7(2)	Cl(4)-Cu(2)-N(7)	90.76(19)
O(5)-Cu(1)-N(1)	88.3(3)	O(6)-Cu(2)-N(6)	84.9(2)
O(5)-Cu(1)-N(12)	90.9(3)	O(6)-Cu(2)-N(7)	86.1(2)
N(1)-Cu(1)-N(12)	176.3(3)	N(6)-Cu(2)-N(7)	170.7(3)
N(3)-C(7)-C(8)-O(1)		-71.0(10)	
N(9)-C(25)-C(26)-O(3)		-68.7(8)	
O(4)-C(29)-C(30)-N(10)		65.7(7)	
O(2)-C(11)-C(12)-N(4)		65.4(10)	

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
C(7)–H(7B)···Cl(2)^{i}	0.97	2.70	3.523(8)	143
C(11)–H(11B)···Cl(3)^{ii}	0.97	2.79	3.538(10)	134
C(12)–H(12B)···O(2)^{i}	0.97	2.53	3.500(11)	171
C(25)–H(25B)···Cl(2)^{i}	0.97	2.69	3.562(7)	150
C(29)–H(29B)···Cl(3)^{ii}	0.97	2.77	3.560(8)	139
C(30)–H(30A)···Cl(4)^{i}	0.97	2.78	3.667(7)	152
C(37)–H(37)···N(11)	0.93	2.50	3.076(14)	120
C(42)–H(42A)···O(6)	0.96	2.45	2.817(12)	103

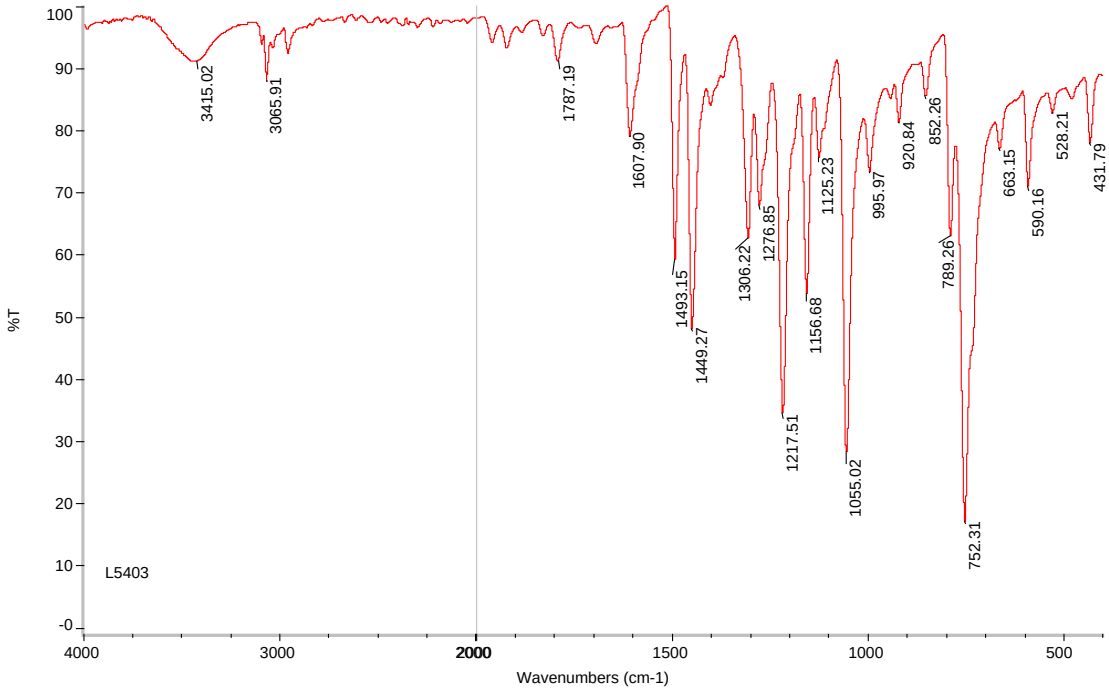
π···π Interactions□Face-to-Face□

Cg(a)–Cg(b)	dihedral angle (a,b) (°)	Ring Centroids Distance (Å)
Cg(1)–Cg(5)^{iii}	1.14	3.668(5)
Cg(2)–Cg(6)^{iii}	0.64	3.840(4)
Cg(3)–Cg(8)^{iv}	0.81	3.784(5)
Cg(4)–Cg(7)^{iv}	0.20	3.722(5)

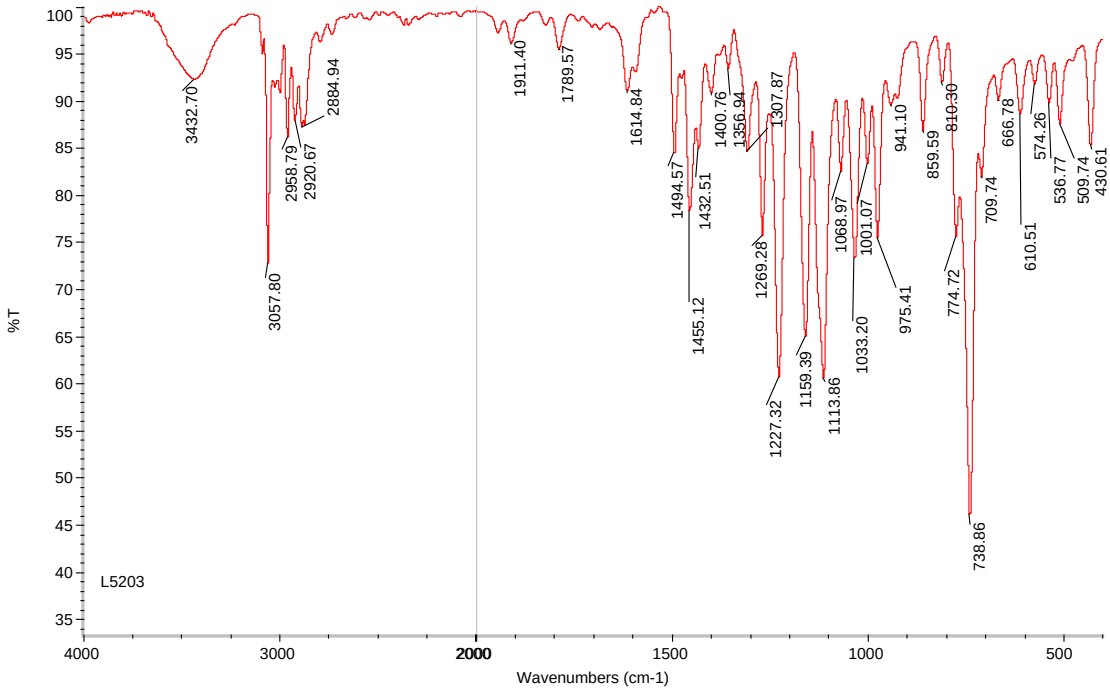
Symmetry codes: i) x, 1/2-y, -1/2+z; ii) x, 1/2-y, 1/2+z; iii) x, 1/2-y, -1/2+z; iv) 1/2-x, -y, -1/2+z; Ring Cg(1): N(1)–N(2)–N(3)–C(6)–C(1); Ring Cg(2): N(4)–N(5)–N(6)–C(18)–C(13); Ring Cg(3): N(7)–N(8)–N(9)–C(24)–C(19); Ring Cg(4): N(10)–N(11)–N(12)–C(36)–C(31); Ring Cg(5): C(1)–C(2)–C(3)–C(4)–C(5)–C(6); Ring Cg(6): C(13)–C(14)–C(15)–C(16)–C(17)–C(18); Ring Cg(7):

C(19)–C(20)–C(21)–C(22)–C(23)–C(24); Cg(8):
C(31)–C(32)–C(33)–C(34)–C(35)–C(36).

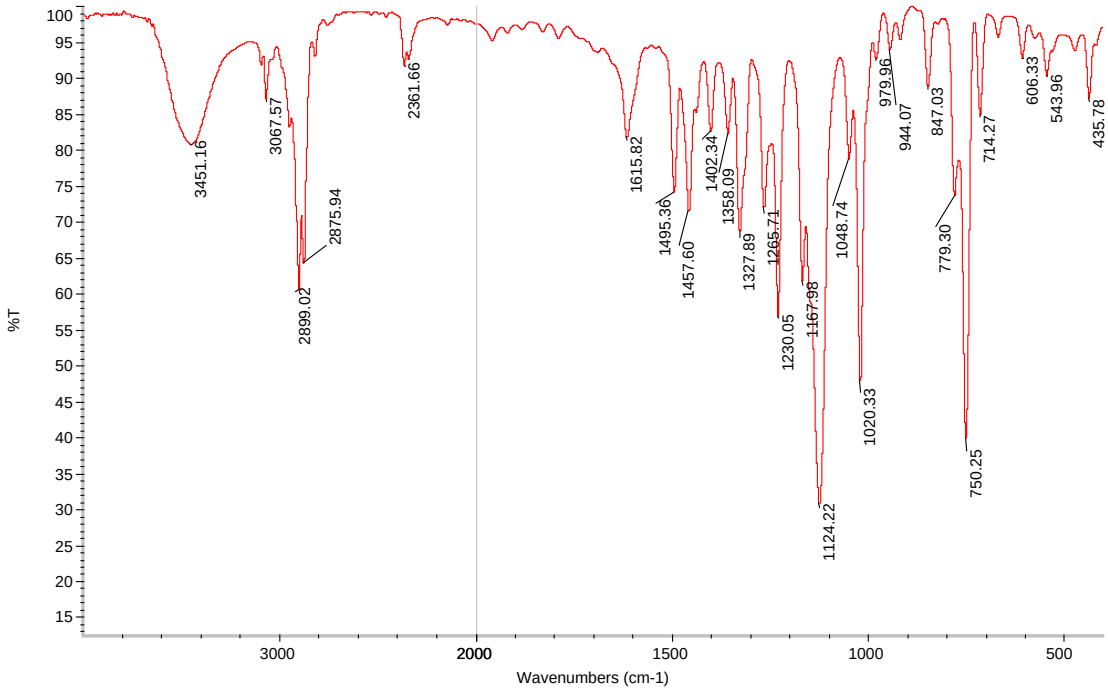
Fig. S1 IR of the ligands L^1, L^2 and L^3



Ligand L^1

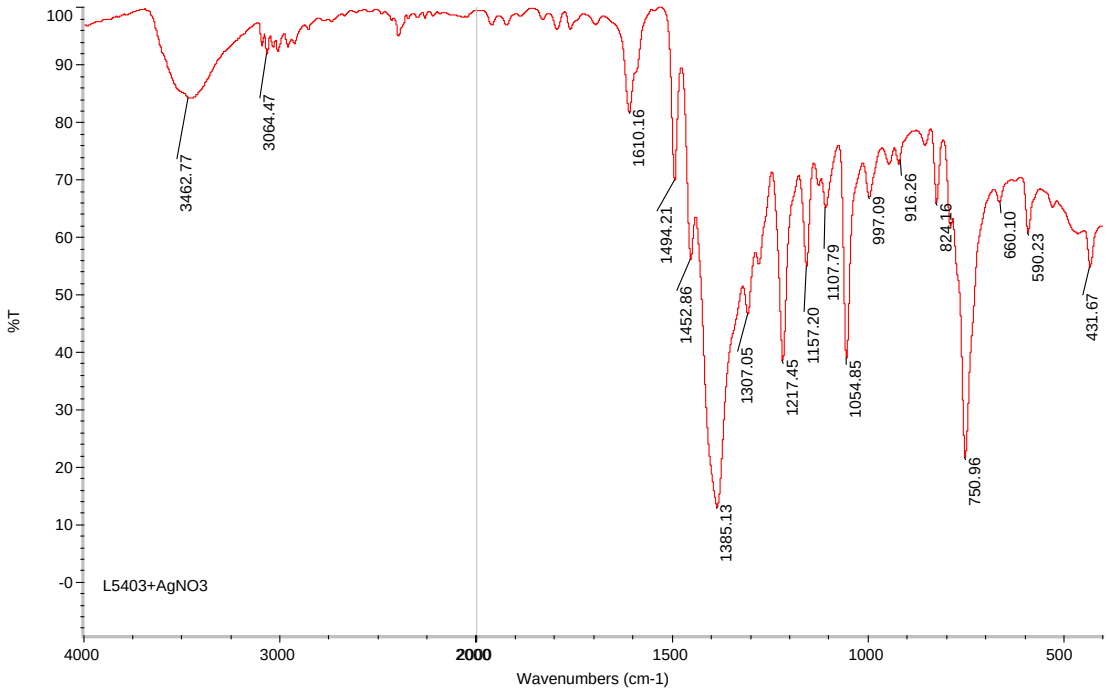


Ligand L^2

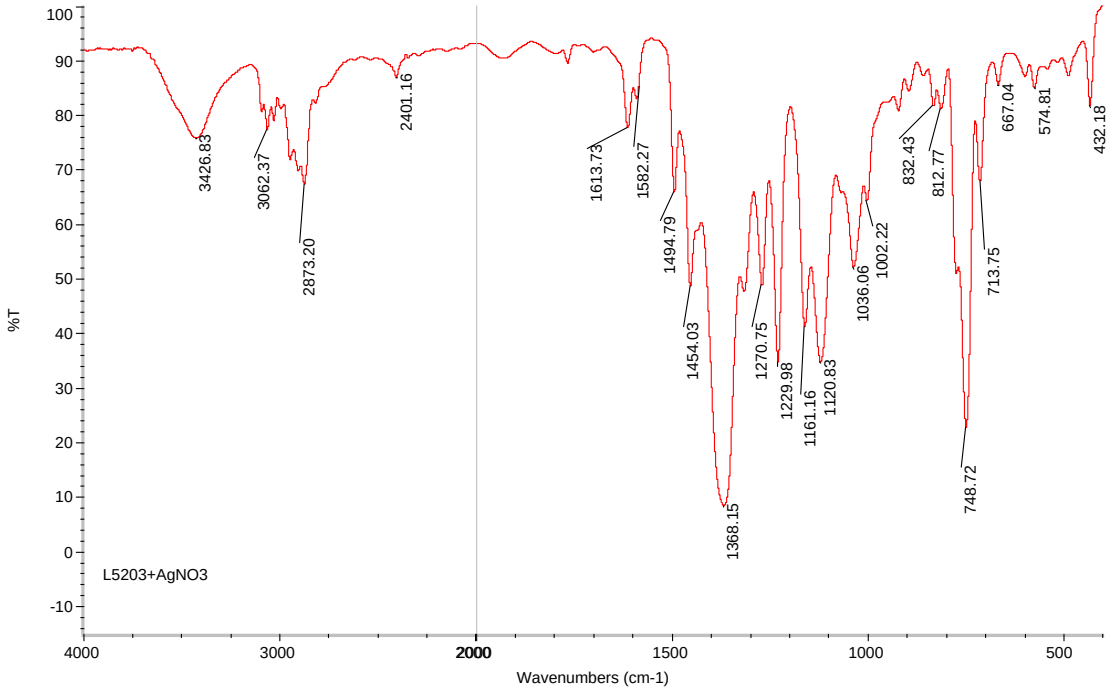


Ligand L^3

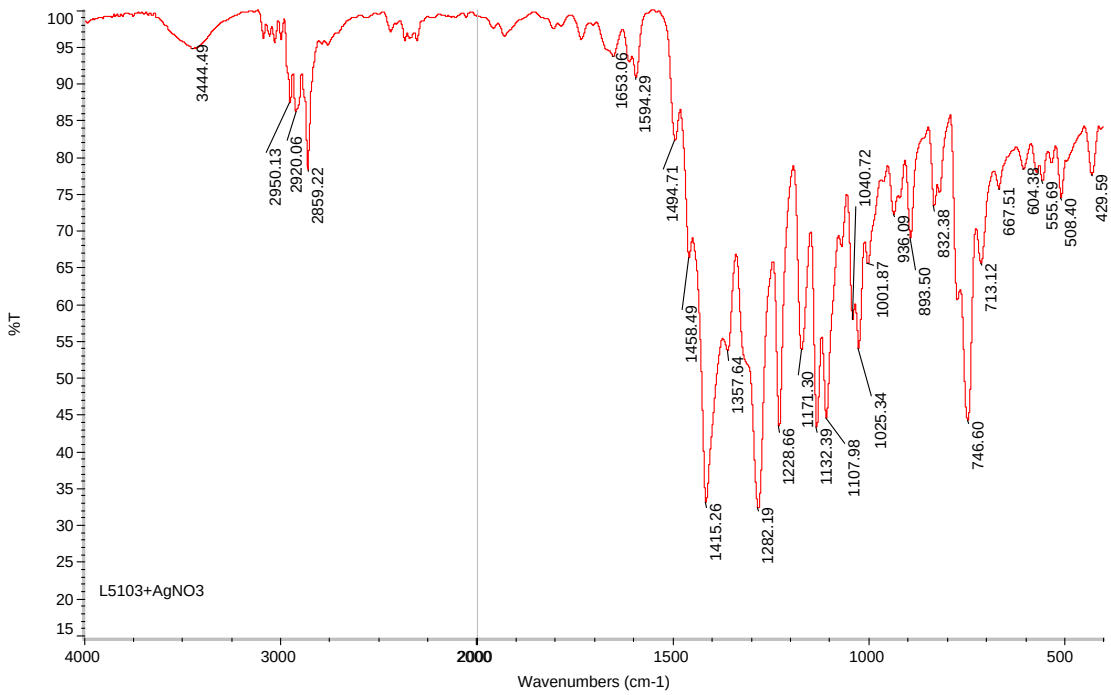
Fig. S2 IR of the complexes **1**−**6**.



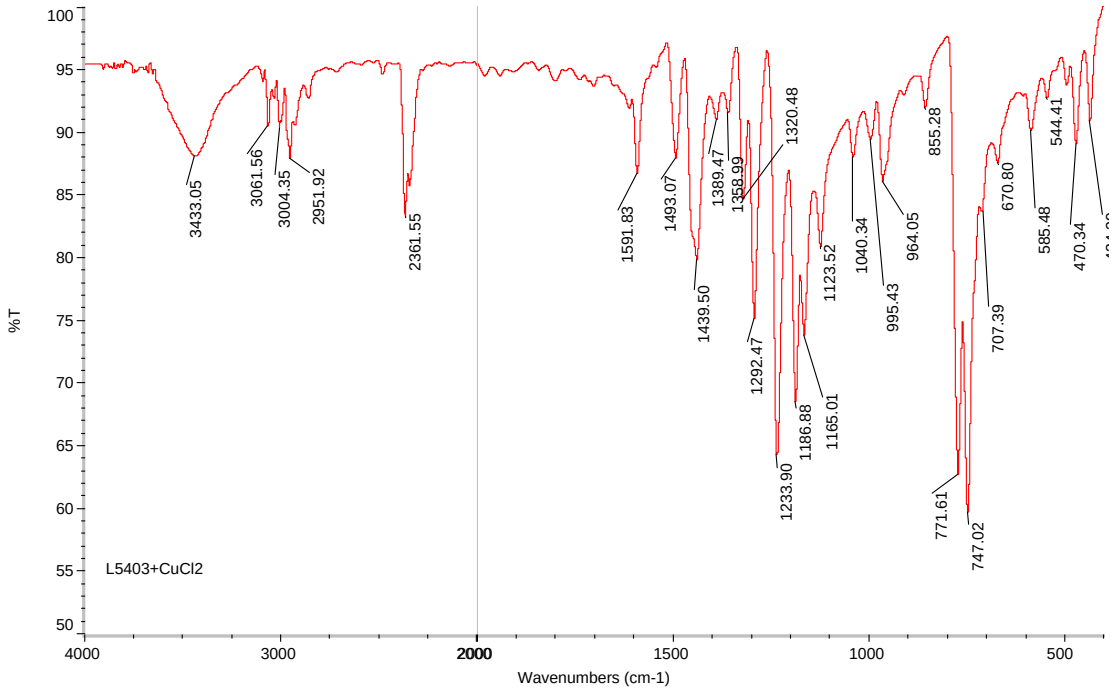
Complex 1



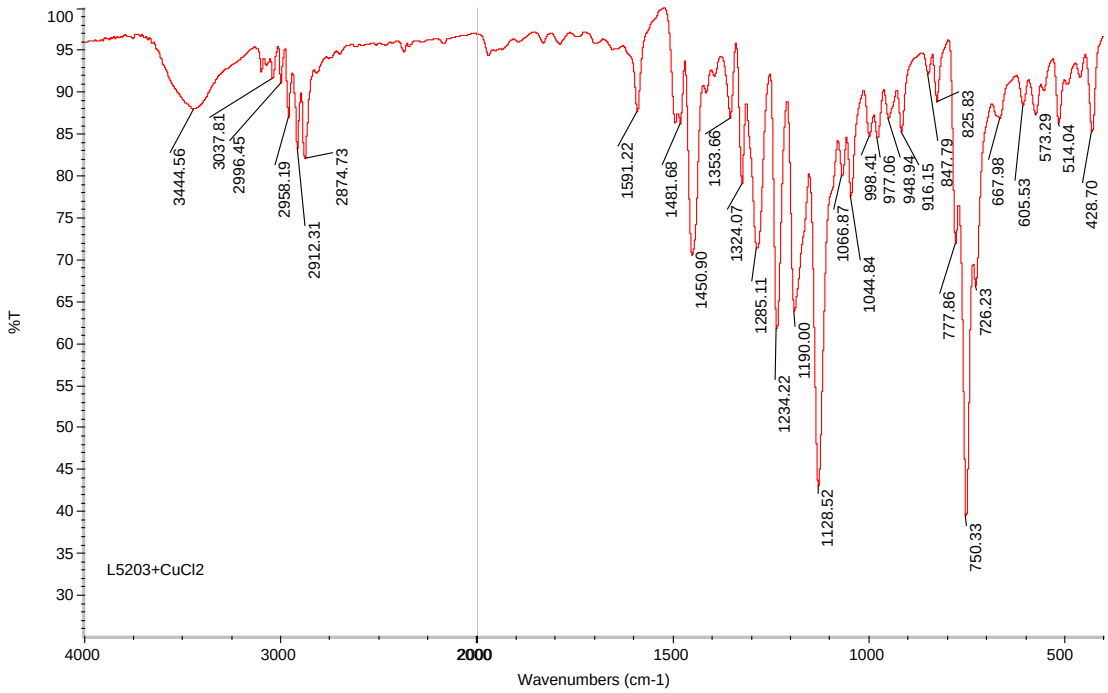
Complex 2



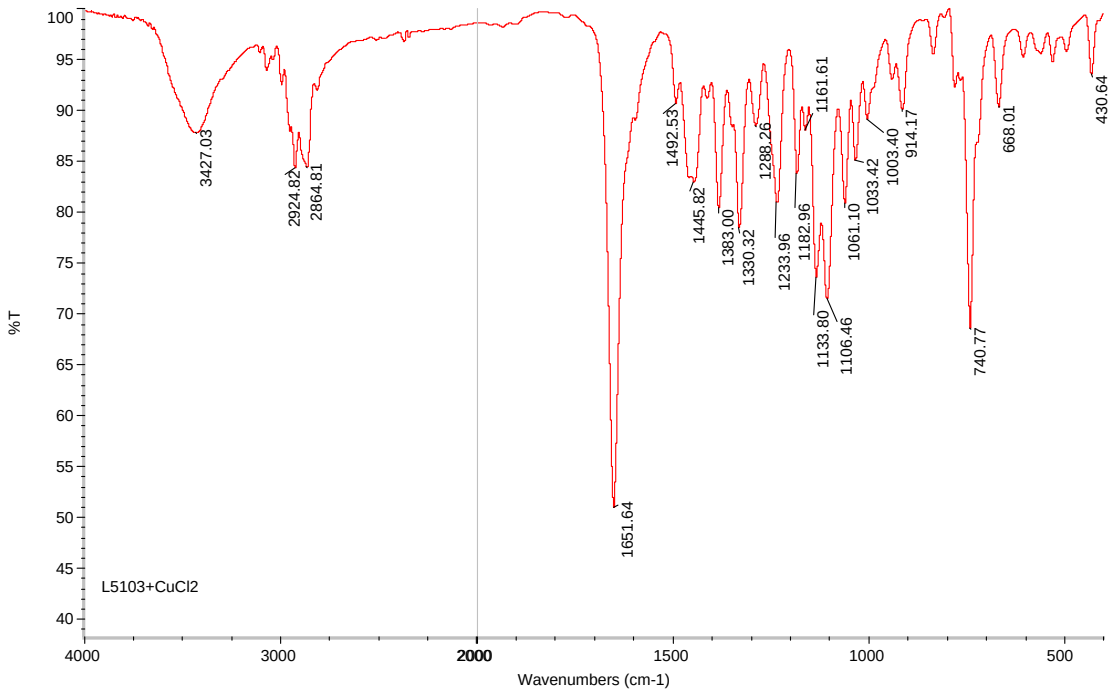
Complex 3



Complex 4



Complex 5



Complex 6