Suplementary information for

Metal self-recognition: a pathway to control the formation of dihelicates and mesocates

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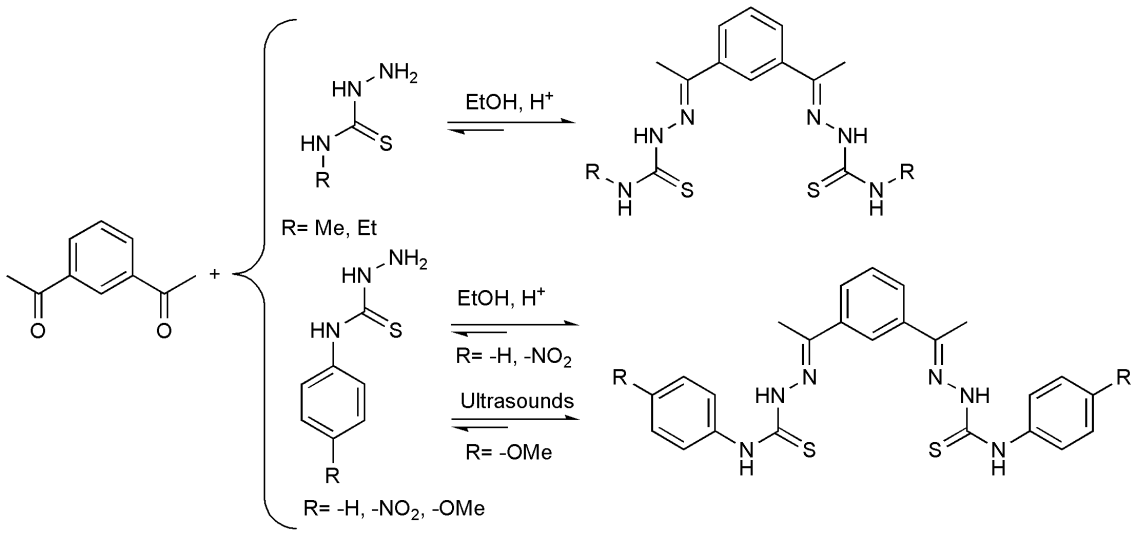
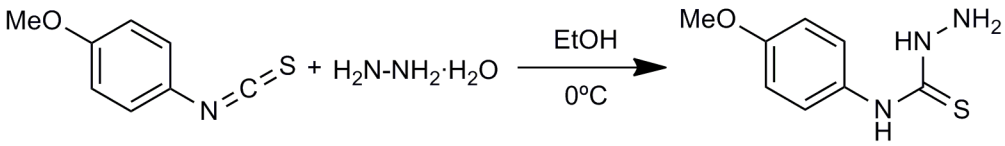
S1. Schemes



Scheme S1. Synthesis of the thiosemicarbazone ligands H_2L^R.



Scheme S2. Synthesis of the thiosemicarbazide precursor H_2PhOMe.

S2. Figures

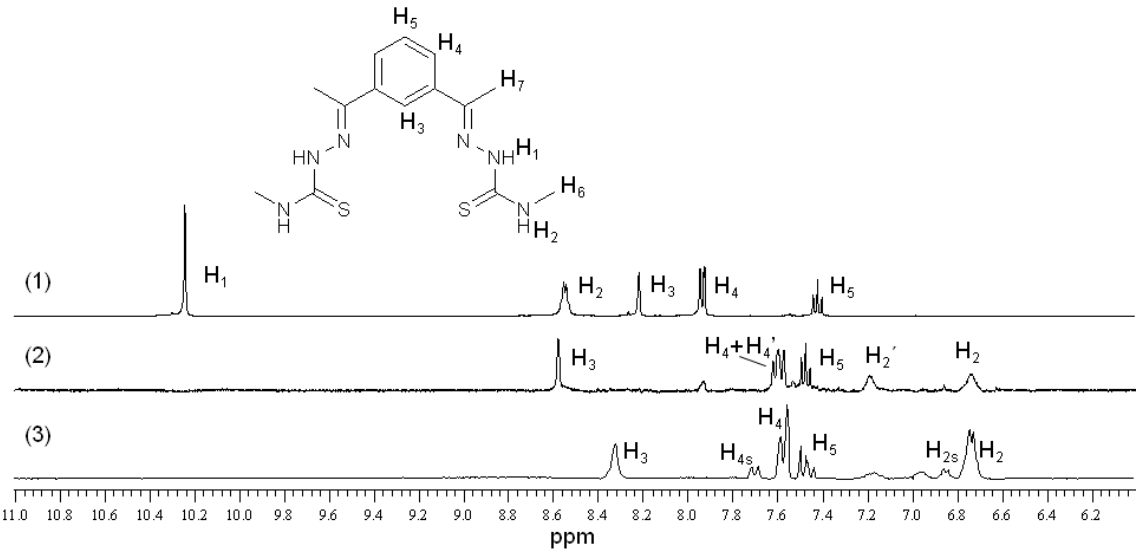


Figure S1. Superposition of aromatic region of ^{1}H NMR spectra of (1) H_2L^{Me}, (2) $[Zn_2(L^{Me})_2]^{i}$ and (3) $[Cd_2(L^{Me})_2]$

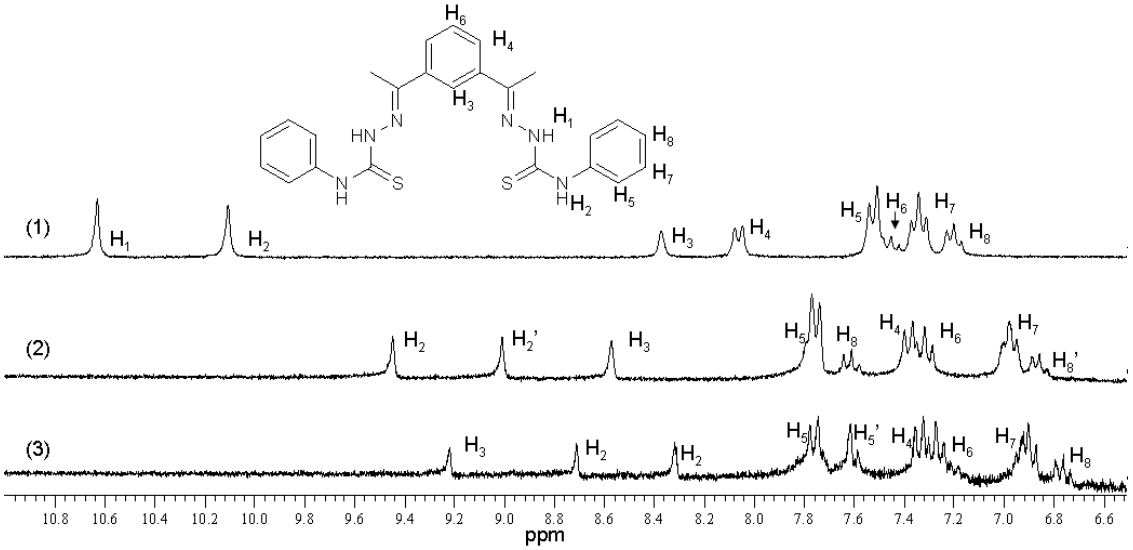


Figure S2. Superposition of aromatic region of ^{1}H NMR spectra of (1) H_2L^{Ph}, (2) $[Zn_2(L^{Ph})_2]\cdot 2H_2O$ and (3) $[Cd_2(L^{Ph})_2]\cdot 2H_2O^{ii}$

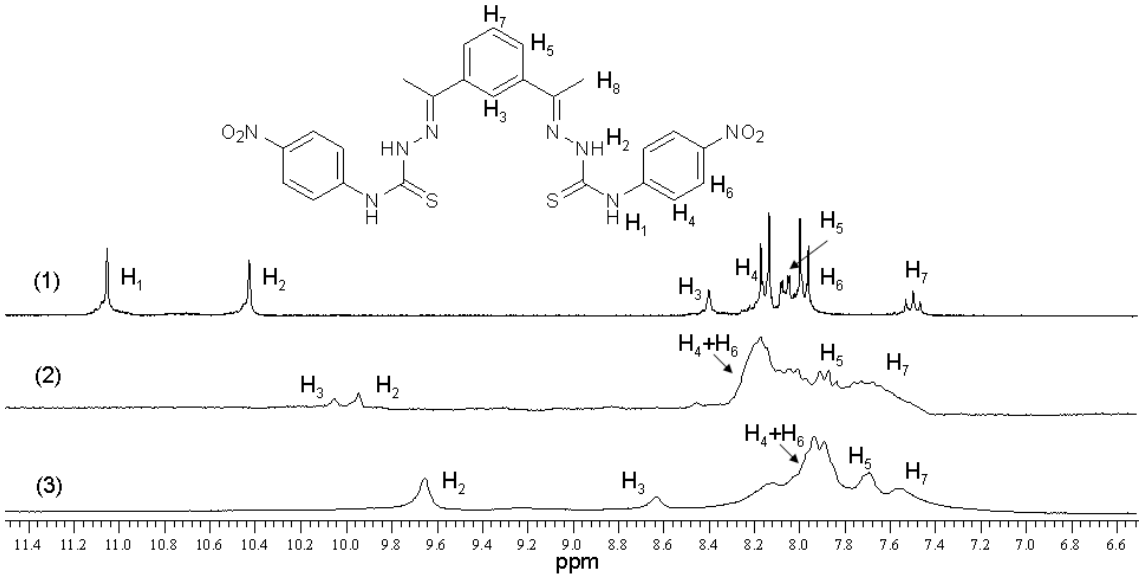


Figure S3. Superposition of aromatic region of ^{1}H NMR spectra of (1) H_2L^{PhN}, (2) $[Zn_2(L^{PhN})_2]\cdot 3H_2O$ and (3) $[Cd_2(L^{PhN})_2]\cdot 3H_2O$

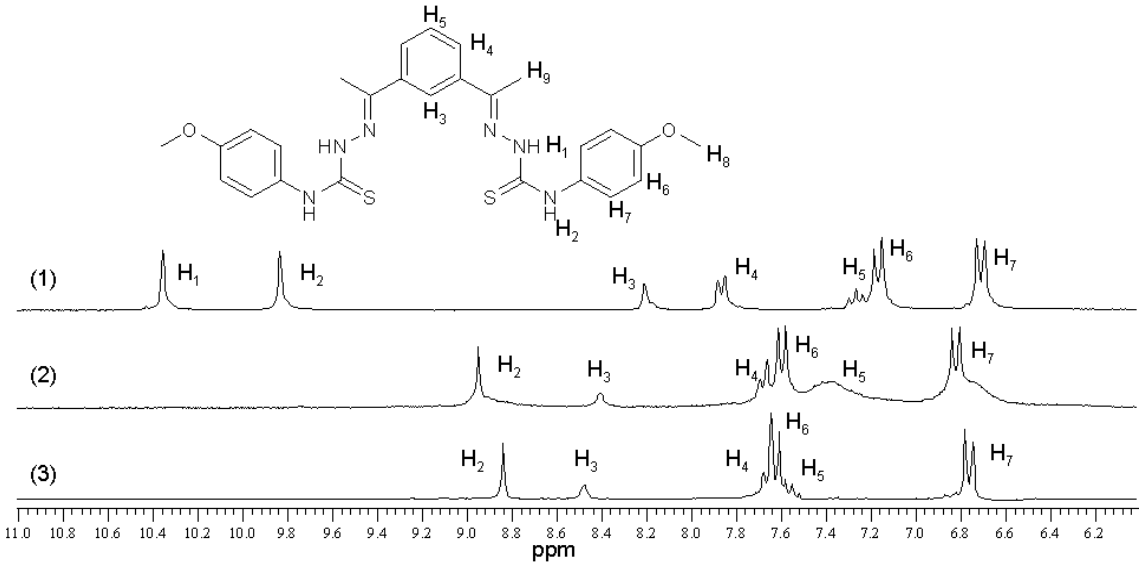


Figure S4. Superposition of aromatic region of ^{1}H NMR spectra of (1) H_2L^{PhOMe}, (2) $[Zn_2(L^{PhOMe})_2]\cdot 2H_2O$ and (3) $[Cd_2(L^{PhOMe})]_2$

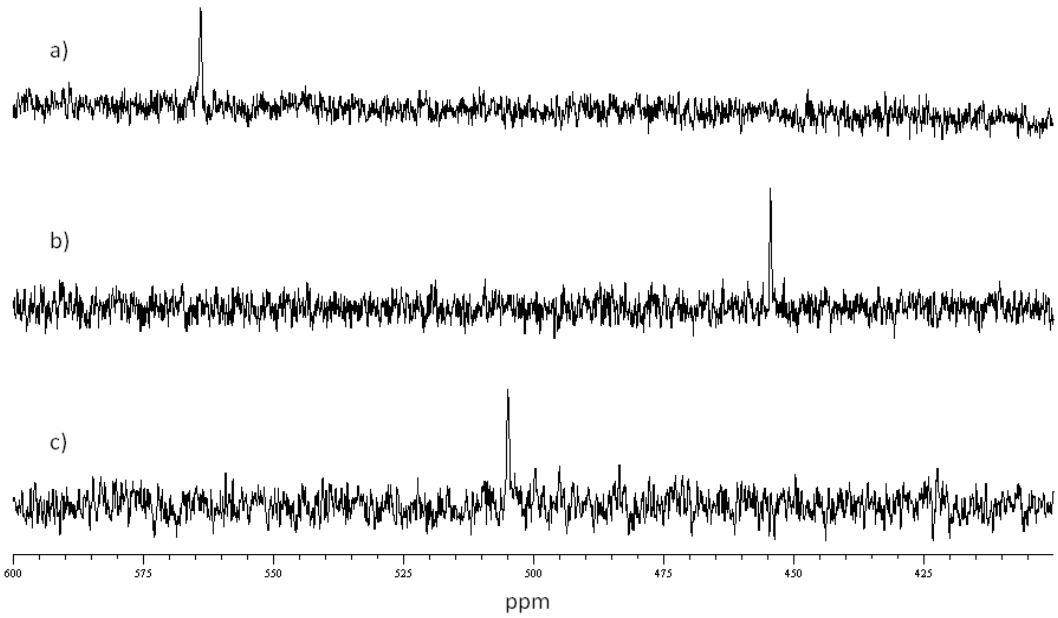


Figure S5. Superposition of the ^{113}Cd NMR (DMSO-d_6) spectra of complexes a) $[Cd_2(L^{Et})_2]\cdot H_2O$, b) $[Cd_2(L^{PhOMe})_2]$ and c) $[Cd_2(L^{PhN})_2]\cdot 3H_2O$.

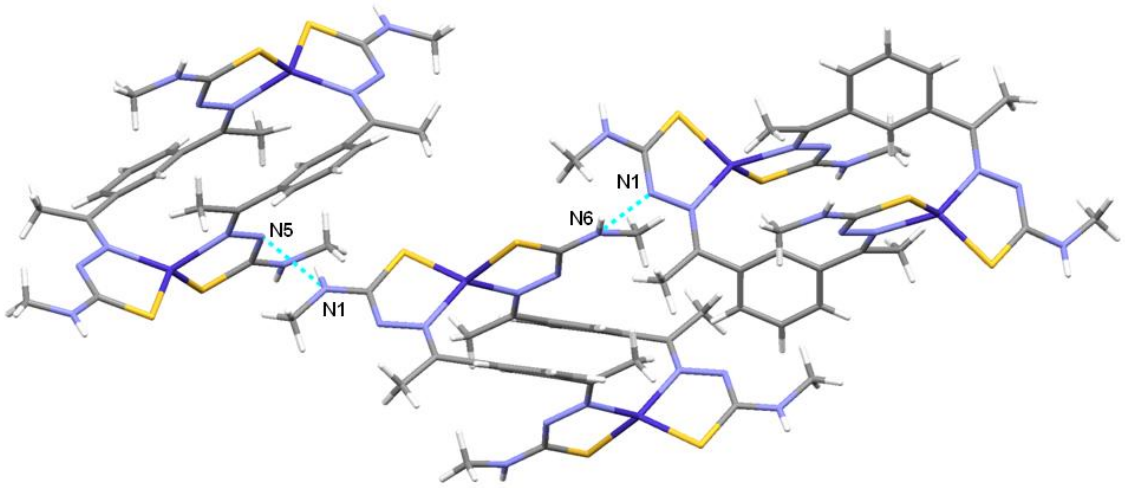


Figure S6. H-bonds established in the crystal network of complex **1**.

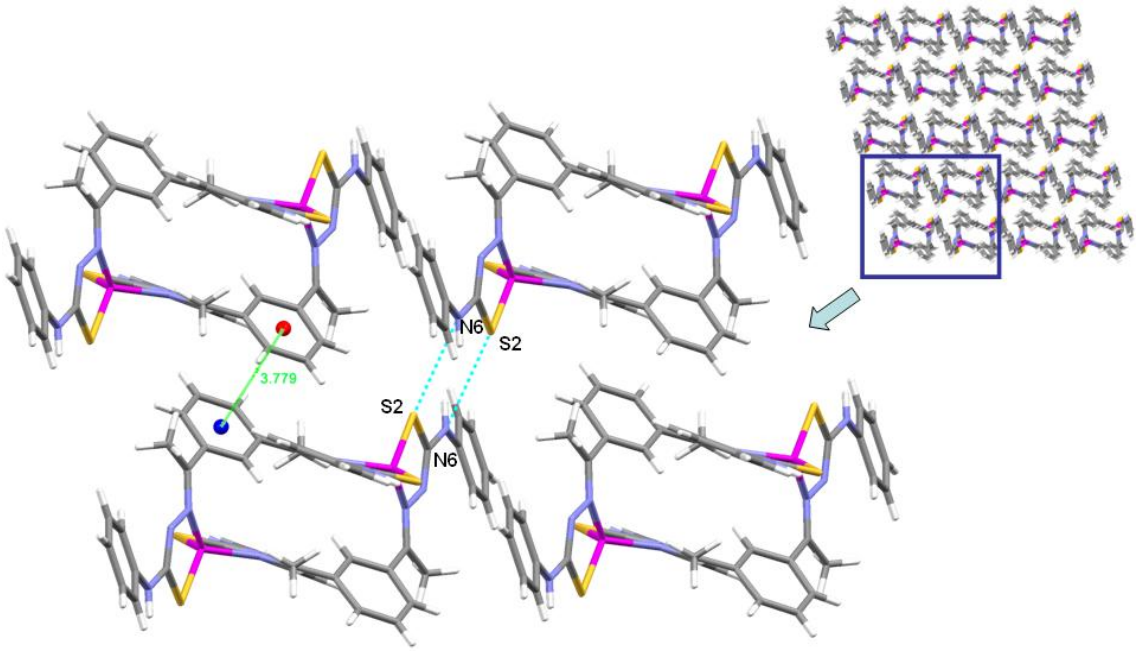


Figure S7. No covalent interactions and packing of mesocate $[Zn_2(L^{Ph})_2]\cdot 2CHCl_3$ **3**.

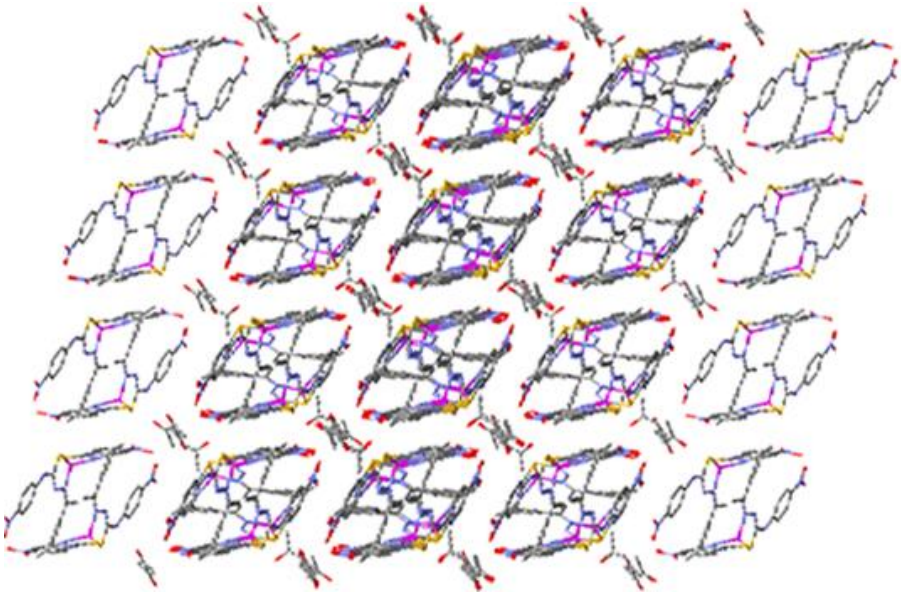


Figure S8. Packing of mesocate $[Zn_2(L^{PhN})_2]_2\cdot 5(CH_3)_2CO$ **4.**

S3. Tables

Table S1. Main Crystallographic data of H_2L^{Me}.

Formula	$C_{14}H_{20}N_6S_2$	**Volume/Å^3**	829.13(7)
Molecular weight	336.49	**Z**	2
Space group	P-1	**D/g cm^{-3}**	1.348
Crystal system	Triclinic	**Interval θ/º**	1.95 to 26.54
Crystal size /mm	0.87 x 0.20 x 0.08	**Measured reflexions**	18961
a/Å	5.4234(3)	**Independent reflexions [R_{int}]**	3424 [0.0434]
b/Å	10.6842(5)	**μ /mm^{-1}**	0.327
c/Å	14.7858(7)	**F(000)**	356
α/º	77.839(2)	**Residues/e Å^{-3}**	0.32 and -0.28
β/º	81.951(3)	**R Final index [I>2sigma(I)]**	0.0384 [0.0903]
γ/º	87.250(2)	**R index [all data]**	0.0578 [0.0972]

Table S2. Hydrogen bonds in the crystal lattice of H_2L^{Me}.

D-H···A	D···A (Å)	D-H···A (º)	Symmetry operation
N1-H1N···N3	2.612 (2)	109.5(17)	
N6-H6N···N4	2.604 (3)	111.1(17)	
C6-H6···N3	2.763 (3)	98.9	
C10-H10···N4	2.761 (2)	99.6	
N2-H2N···S1	3.6220 (19)	160(2)	-x+2, -y+1, -z+1
N5-H5N···S2	3.6913 (18)	169.6(18)	-x-2, -y+1, -z+2

Table S3. Selected bond distances (Å) and angles (º) of H_2L^{Me}.

Bond distances (Å)					
C1-N1	1.449(3)	C5-C6	1.410(3)	C12-N4	1.290(2)
C2-N1	1.332(3)	C6-C7	1.374(3)	C13-N6	1.329(2)
C2-N2	1.364(2)	C7-C8	1.392(3)	C15-N5	1.364(2)
C2-S1	1.678(2)	C8-C9	1.393(3)	C13-S2	1.683(2)
C3-C4	1.497(3)	C9-C10	1.401(3)	C14-N6	1.448(2)
C4-N3	1.290(2)	C9-C12	1.484(3)	N2-N3	1.374(2)
C4-C5	1.483(3)	C11-C12	1.497(2)	N4-N5	1.371(2)
C5-C10	1.390(2)				
Bond angles (º)					
N1-C2-N2	115.89(17)	C6-C7-C8	120.69(17)	N6-C13-N5	115.85(17)
N1-C2-S1	123.82(15)	C7-C8-C9	120.52(18)	N6-C13-S2	124.48(14)
N2-C2-S1	120.29(15)	C8-C9-C10	118.14(17)	N5-C13-S2	119.67(14)
N3-C4-C5	115.59(16)	C8-C9-C12	121.30(17)	C2-N1-C1	123.55(18)
N3-C4-C3	124.45(17)	C10-C9-C12	120.53(16)	C2-N2-N3	118.96(17)
C5-C4-C3	119.92(16)	C5-C10-C9	122.13(17)	C4-N3-N2	118.82(16)
C10-C5-C6	118.13(17)	N4-C12-C9	115.60(16)	C12-N4-N5	118.38(16)
C10-C5-C4	121.15(16)	N4-C12-C11	123.90(17)	C13-N5-N4	118.51(16)
C6-C5-C4	120.71(16)	C9-C12-C11	120.49(16)	C13-N6-C14	124.57(16)
C7-C6-C5	120.36(17)				

Table S4. Main crystal data of $[Co_2(L^{Me})_2]$ **1**.

Formula	$Co_2C_{28}H_{36}N_{12}S_4$	**Volume/Å^3**	3582.93 (6)
Molecular weight	786.83	**Z**	4
Space group	Pbca	**D/g cm^{-3}**	1.459
Crystal system	Ortorombic	**Interval θ/º**	2.31- 26.36
Crystal size /mm	0.13 x 0.08 x 0.05	**Measured reflexions**	19797
a/Å	14.4792(13)	**Independent reflexions [R_{int}]**	2206 [0.0938]
b/Å	15.5345(14)	**μ /mm^{-1}**	198
c/Å	15.9289(15)	**F(000)**	1624
α/º	90	**Residues/e Å^{-3}**	1.005 and -0.705
β/º	90	**R Final index [I>2sigma(I)]**	0.0759 [0.1763]
γ/º	90	**R index [all data]**	0.1303 [0.1982]

Table S5. Main bond distances **(Å)** and angles **(º)** of $[Co_2(L^{Me})_2]$ **1**.

Bond distances (Å)		**Bond angles (º)**	
Co1-N4	2.033(5)	N4-Co1-N3	126.9(2)
Co1-N3	2.078(6)	N4-Co1-S2	86.13(14)
Co1-S2	2.270(2)	N3-Co1-S2	115.09(14)
Co1-S1	2.272(2)	N4-Co1-S2	122.32(16)
		N3-Co1-S2	85.65(17)
		S1-Co1-S2	125.36(8)

Table S6. Intermolecular hydrogen bonds in the crystal lattice of $[Co_2(L^{Me})_2]$ **1**.

D-H···A	**D···A (Å)**	**D-H···A (º)**	**Symmetry operation**
N1-H1N···N5	3.046(7)	145(5)	½-x, ½+y, z
N6-H6N···N2	3.342(9)	151(6)	-x, -½+y, ½-z

Table S7. Crystal data of $[Zn_2(L^{Et})_2]$ **2**, $[Zn_2(L^{Ph})_2]$ $2CHCl_3$ **3**, $[Zn_2(L^{PhN})_2]_2 \cdot 5(CH_3CO)$ **4** and $[Zn_2(L^{PhOMe})_2]$ **5**.

	2	**3**	**4**	**5**
Formula	$C_{32}\ H_{44}\ N_{12}\ S_4\ Zn_2$	$C_{48}H_4\ N_{12}S_4Zn_2,\ 2(CHCl_3)$	$2(C_{48}H_{40}N_{16}O_8S_4Zn_2)\cdot 5(C_3H_6O)$	$C_{52}H_{52}N_{12}O_4S_4Zn_2$
Molecular weight	855.67	1286.75	2746.43	1168.12
Space group	P21/n	P-1	P-1	P-1
Crystalline system	Monoclinic	Triclinic	Triclinic	Triclinic
Crystal size /mm	0.10 x 0.08 x 0.05	0.15 x 0.09 x 0.03	0.07 x 0.07 x 0.01	0.13 x 0.08 x 0.02
a/Å	10.6969(4)	8.9266(2)	11.1425(7)	8.9413(3)
b/Å	14.6726(5)	12.5924(3)	15.4703(10)	12.1646(4)
c/Å	11.8716(4)	13.3789(3)	18.6236(11)	13.6340(5)
α/º	90	107.083(1)	97.906(3)	65.614(2)
β/º	90.6800(10)	104.056(1)	91.450(2)	76.570(2)
γ/º	90	99.236(1)	107.563(2)	70.636(2)
Volume/Å^3	1863.13(11)	1350.20(5)	3024.0(3)	1266.36(8)
Z	2	1	1	1
D/g cm^{-3}	1.525	1.582	1.508	1.532
Interval θ/º	2.21-28.3	1.75-28.29	1.11-22.99	1.65-26.03
Measured reflexions	31071	28152	38469	18926
Independent reflexions [R_{int}]	4617[0.066]	6659 [0.054]	8384 [0.138]	4981 [0.054]
μ /mm^{-1}	1.55	1.389	1.004	1.172
F(000)	888	656	1416	604
Residues/e Å^{-3}	0.61 and -0.34	0.572 and -0.777	0.895 and -0.666	0.732 and -0.413
Final R index [I>2sigma(I)]	0.0352[0.0696]	0.0522 [0.1122]	0.0612 [0.0954]	0.0397 [0.0800]
R index [all data]	0.0543[0.0743]	0.1023 [0.1287]	0.1467 [0.1224]	0.0691 [0.0903]

Table S8. Main bond distances (Å) and bond angles (º) of the linkage isomers in **2**.

2 (a)		**2 (b)**	
Bond distances (Å)			
Zn1 N3	2.0477(17)	Zn1C N3	2.051(5)
Zn1 N4_2	2.0670(2)	Zn1C N5B_2	2.010(2)
Zn1 S1	2.3100(7)	Zn1C S1	2.157(5)
Zn1 S2_2	2.2763(7)	Zn1C S2B_2	2.392(8)
Bond angles (º)			
N3 Zn1 N4_2	119.71(7)	N5B Zn1C N3_2	118.9(6)
N4 Zn1 S1_2	118.97(6)	N5B Zn1C S1 _2	121.8(6)
N3 Zn1 S1	85.72(5)	N3 Zn1C S1	89.76(19)
N4 Zn1 S2_2	87.22(6)	N5B Zn1C S2B_2	71.6(6)
N3 Zn1 S2_2	121.51(5)	N3 Zn1C S2B_2	123.4(3)
S1 Zn1 S2_2	127.75(3)	S1 Zn1C S2B_2	134.7(3)

Table S9. Main bond distances (Å) and angles (º) of mesocates **3** and **5**.

	3	**5**
Bond distances (Å)		
Zn1-N3	2.074(3)	2.061(2)
Zn1-N4_2	2.052(3)	2.073(2)
Zn1-S1	2.2516(11)	2.2793(8)
Zn1-S2_2	2.2907(10)	2.2880(8)
Bond angles (º)		
N4_2-Zn1-N3	125.87(11)	128.57(10)
N4_2-Zn1-S1	120.84(8)	114.33(7)
N3-Zn1-S1	87.23(8)	86.98(7)
N4_2-Zn1-S2_2	86.31(8)	86.63(7)
N3-Zn1-S2_2	115.53(8)	117.79(7)
S1-Zn1-S2_2	125.46(4)	127.46(3)

Table S10. Main bond distances (Å) and bond angles (º) of the conformational isomers of **4**.

4 (a)		**4 (b)**	
Bond distances (Å)			
Zn1-N4	2.072(5)	Zn2-N12	2.061(5)
Zn1-N5_2	2.054(5)	Zn2-N13_3	2.076(5)
Zn1-S1	2.257(2)	Zn2-S3	2.276(2)
Zn1-S2_2	2.276(2)	Zn2-S4_3	2.258(2)
Bond angles (º)			
N5_2-Zn1-N4	122.6(2)	N12-Zn2-N13_3	122.3(2)
N5_2-Zn1-S1	123.62(17)	N12-Zn2-S4_3	123.70(16)
N4-Zn1-S1	87.62(17)	N13_2-Zn2-S4_3	87.55(16)
N5_2-Zn1-S2_2	86.44(17)	N12-Zn2-S3	85.71(17)
N4-Zn1-S2_2	117.96(16)	N13_3-Zn2-S3	116.86(16)
S1-Zn1-S2_2	122.61(8)	S4_3-Zn2-S3	124.76(8)

Table S11. Intermolecular hydrogen bonds in the crystal lattice of **2**, **3**, **4** and **5**.

Complex	**D-H···A**	**D···A (Å)**	**D-H···A (º)**	**Symmetry operation**
2	N1 H1N ···N5	3.051(3)	149(2)	1.5-X, -0.5+Y, -0.5-Z
3	N6 H6N··· S2	3.384(3)	144(4)	2-x, 2-y, 2-z
4	N2-H2···O10	2.928 (8)	169.1	x, y, z
	N7-H7···S3	3.405 (6)	135.2	x, y, z
	N7-H7···O11	2.988 (13)	140.5	x, y, z
	N10-H10···S2	3.493 (6)	162.7	x, y, z
	N15-H15···O9	2.873 (7)	161.8	-x+1, -y, -z+1
5	N1-H1···S2	3.639 (3)	156(3)	-1+x, 1+y, z

Table S12. Main crystal data of **6**.

	6
Formula	$C_{48}H_{40}Cd_2N_{16}O_8S_4$, $4(C_2H_6OS)$
Molecular weight	1634.51
Space group	Pna21
Crystalline system	Triclinic
Crystal size /mm	0.50 x 0.13 x 0.04
a/Å	30.0597(13)
b/Å	8.3317(4)
c/Å	27.4037(12)
α/º	90
β/º	90
γ/º	90
Volume/Å^3	6863.2(5)
Z	4
D/g cm^{-3}	1.582
Interval θ/º	1.49- 26.37
Measured reflexions	108959
Independent reflexions [R_{int}]	13806 [0.056]
μ /mm^{-1}	0.933
F(000)	3328
Residues/e Å^{-3}	1.218 and -0.440
Final R index [I>2sigma(I)]	0.0359 [0.0664]
R index [all data]	0.0463 [0.0705]

Table S13. Main bond distances (Å) and angles (º) of **6**.

6			
N4-Cd1	2.334(3)	N5-Cd2	2.307(3)
N12-Cd1	2.346(3)	N13-Cd2	2.318(3)
S1-Cd1	2.4653(10)	S2-Cd2	2.4490(10)
S3-Cd1	2.4586(11)	S4-Cd2	2.4552(10)
N4-Cd1-N12	130.19(10)	N5-Cd2-N13	138.16(10)
N4-Cd1-S3	118.34(8)	N5-Cd2-S2	80.02(8)
N12-Cd1-S3	79.10(7)	N13-Cd2-S2	115.40(8)
N4-Cd1-S1	79.40(8)	N5-Cd2-S4	112.93(8)
N12-Cd1-S1	112.10(7)	N13-Cd2-S4	79.38(8)
S3-Cd1-S1	146.71(3)	S2-Cd2-S4	142.30(4)

Table S14. Hydrogen bonds in the crystal lattice of **6**.

Complex	**D-H···A**	**D···A (Å)**	**D-H···A (º)**	**Symmetry operation**
18	N2-H2···O9	2.932 (5)	158(5)	x-1/2, 1/2-y,+z-1
	N10-H10···O10	2.956 (5)	167(4)	x-1/2, 1/2 -y, z
	N7-H7···O12	2.859 (5)	167(4)	x-1/2, 3/2-y, z
	N15-H15···O11	2.895 (5)	163(4)	x-1/2, 3/2-y, z

References

[i] M. R. Bermejo, A. M. González-Noya, M. Martínez-Calvo, R. Pedrido, M. J. Romero, M. Vázquez López, *Eur. J. Inorg. Chem*., 2008, 3852.
[ii] M. Martínez-Calvo, A. M. González-Noya, R. Pedrido, María J. Romero, M. I. Fernández, G. Zaragoza and M. R. Bermejo, *Dalton Trans.*, 2010, **39**, 1191.