

Structural, MALDI-TOF-MS, Magnetic and Spectroscopic Studies of New Dinuclear Copper(II), Cobalt(II) and Zinc(II) Complexes Containing a Biomimicking m-OH bridge.

Cristina Núñez,^{1a} Rufina Bastida,^{*1} Alejandro Macías,¹ Laura Valencia,² Nicolás I. Neuman,³ Alberto C. Rizzi,³ Carlos D. Brondino,^{*3} Pablo J. González,⁴ José Luis Capelo,^{4,5} Carlos Lodeiro,^{*4,5}

¹Departamento de Química Inorgánica, Facultad de Química, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, España.

²Departamento de Química Inorgánica, Facultad de Química, Universidade de Vigo, 36310, Vigo, Pontevedra, España.

³Departamento de Física, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral, Ciudad Universitaria, Paraje el Pozo, S3000ZAA Santa Fe, Argentina.

⁴REQUIMTE-CQFB, Departamento de Química, FCT-Universidade NOVA de Lisboa, 2829 Monte de Caparica, Portugal.

⁵Grupo BIOSCOPE, Departamento de Química Física, Facultad de Ciencias, Universidade de Vigo, Campus de Ourense, E32004 Ourense, España.

**Authors to whom correspondence should be addressed.*

E-mail: mrufina.bastida@usc.es (R.B.)

E-mail: brondino@fbcb.unl.edu.ar (C.D. B.)

E-mail: clodeiro@uvigo.es (C. L.)

Keywords: Copper(II) complexes, Cobalt(II) complexes, Zn(II), macrocycle, EPR, Thiamacrocycles.

Supporting Information

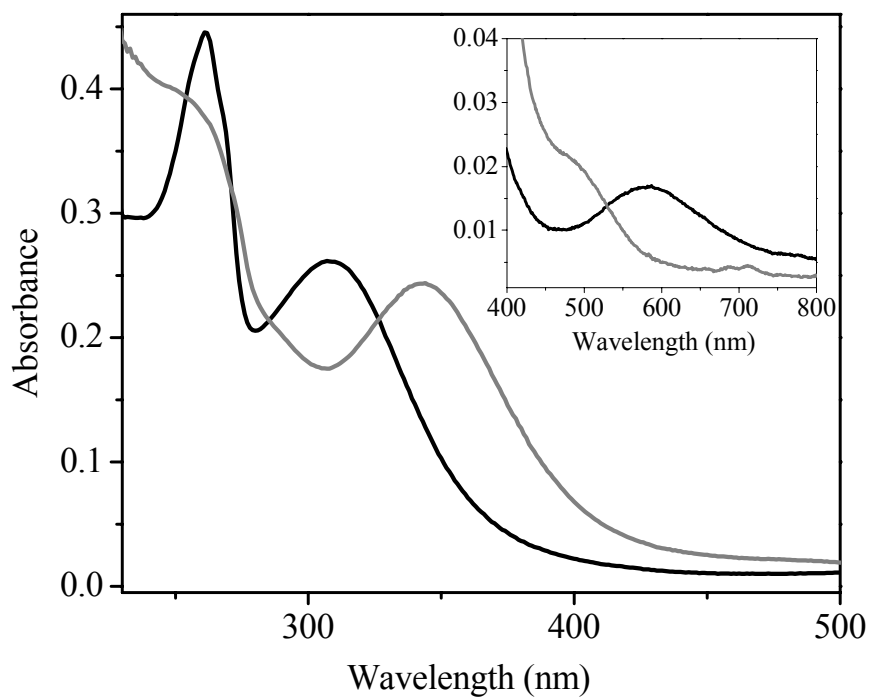


Figure S1. UV-vis spectra of an ethanolic solution of **[Co₂L](BF₄)₄·8H₂O (1)** (gray line) and **[Cu₂L](BF₄)₄·4H₂O (2)** (black line)

Table S1. Possible hydrogen bond distances and angles for **7**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(1W)	0.74(3)	2.09(3)	2.821(2)	170(3)
O(1W)-H(1W)...F(3)	0.80(3)	1.96(3)	2.754(2)	172(2)
O(1W)-H(2W)...F(6)	0.76(3)	2.36(3)	3.0604(19)	154(3)
N(2)-H(2N)...F(1)#1	0.86(2)	2.16(2)	2.9304(19)	149(2)
N(3)-H(3N)...F(3)	0.84(2)	2.26(2)	3.017(2)	150(2)
N(5)-H(5N)...F(4)#1	0.83(2)	2.47(2)	3.135(2)	138(2)
N(6)-H(6N)...O(1W)	0.87(2)	2.32(2)	3.076(2)	146(2)

Table S2. Possible hydrogen bond distances and angles for **8**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...O(1N)	1.00(9)	2.31(10)	2.971(12)	123(7)
N(3)-H(3N)...O(2N)	1.09(10)	1.99(10)	3.039(12)	162(8)
N(3)-H(3N)...O(1N)	1.09(10)	2.46(10)	3.369(11)	141(7)
O(1)-H(1O)...O(2W)#2	0.88(17)	1.99(15)	2.80(3)	153(6)
O(1)-H(1O)...O(2W)#3	0.88(17)	1.99(15)	2.80(3)	153(6)

Table S3. Selected bond distances and angles for **7** and **8**.

	7		8
<i>Bond Lengths (Å)</i>			
Cu(1)-O(1)	1.8973(13)	N(1)-Zn	2.101(8)
Cu(1)-N(1)	1.9273(14)	N(2)-Zn	2.211(8)
Cu(1)-N(2)	2.0976(15)	N(3)-Zn	2.177(8)
Cu(1)-N(6)	2.0613(14)	O(1)-Zn	1.970(4)
Cu(1)-S(2)	2.7259(8)	O(1w)-Zn	2.070(6)
Cu(1)-O(4S)	2.9313(15)	O(1n)-Zn	2.647(8)
Cu(2)-O(1)	1.8968(13)		
Cu(2)-N(4)	1.9360(15)		
Cu(2)-N(5)	2.1028(15)		
Cu(2)-N(3)	2.0676(15)		
Cu(2)-S(1)	2.7672(8)		
Cu(2)-O(2S)	2.8068(14)		
<i>Bond Angles (°)</i>			
O(1)-Cu(1)-N(1)	173.57(5)	O(1)-Zn-O(1w)	103.0(3)
O(1)-Cu(1)-N(2)	98.18(5)	O(1)-Zn-N(1)	150.1(3)
N(1)-Cu(1)-N(2)	80.97(6)	O(1w)-Zn-N(1)	106.9(3)
O(1)-Cu(1)-N(6)	96.96(6)	O(1)-Zn-N(3)	97.9(4)
N(1)-Cu(1)-N(6)	82.78(6)	O(1w)-Zn-N(3)	98.6(3)
N(1)-Cu(1)-O(4S)	82.46(5)	N(1)-Zn-N(3)	77.0(3)
O(1)-Cu(2)-N(4)	175.08(5)	O(1)-Zn-N(2)	98.7(4)
O(1)-Cu(2)-N(5)	97.50(5)	O(1w)-Zn-N(2)	101.2(3)
N(4)-Cu(2)-N(5)	81.21(5)	N(1)-Zn-N(2)	76.4(3)
O(1)-Cu(2)-N(3)	98.52(5)	N(3)-Zn-N(2)	150.5(3)
N(4)-Cu(2)-N(3)	82.16(6)		
N(5)-Cu(2)-S(1)	103.98(5)		