Supporting Information

3,3′-Di(pyrazinamoyl)-2,2′-bipyridine: Rational ligand design for the self-assembly of a 1D coordination polymer

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S-1 Ligand L^3H_2- Tables of bond distances and angles

Bond distances (Å)

C1—N1	1.347 (5)	C11—N5	1.342 (5)
C1—C2	1.423 (5)	C11—C12	1.418 (5)
C1—C1^{i}	1.494 (7)	C11—C11^{ii}	1.502 (7)
C2—C3	1.394 (5)	C12—C13	1.393 (5)
C2—N2	1.398 (5)	C12—N6	1.404 (5)
C3—C4	1.367 (5)	C13—C14	1.374 (5)
C4—C5	1.375 (5)	C14—C15	1.373 (5)
C5—N1	1.329 (5)	C15—N5	1.334 (5)
C6—O1	1.223 (4)	C16—O2	1.225 (4)
C6—N2	1.350 (5)	C16—N6	1.345 (5)
C6—C7	1.516 (5)	C16—C17	1.501 (5)
C7—N3	1.338 (5)	C17—N7	1.339 (5)
C7—C8	1.382 (5)	C17—C18	1.386 (5)
C8—N4	1.338 (5)	C18—N8	1.335 (5)
C9—N4	1.339 (5)	C19—N8	1.334 (6)
C9—C10	1.382 (6)	C19—C20	1.393 (6)
C10—N3	1.336 (5)	C20—N7	1.327 (5)

Symmetry code(s): (i) −x, −y+1, −z+1; (ii) −x+1, −y, −z+2.

Bond angles (°)

N1—C1—C2	119.6 (3)	C14—C13—C12	119.6 (3)
N1—C1—C1^{i}	115.4 (4)	C14—C13—H13	120.2
C2—C1—C1^{i}	125.0 (4)	C12—C13—H13	120.2
C3—C2—N2	122.6 (3)	C15—C14—C13	119.7 (3)
C3—C2—C1	117.3 (3)	C15—C14—H14	120.1
N2—C2—C1	120.1 (3)	C13—C14—H14	120.1
C4—C3—C2	121.3 (3)	N5—C15—C14	121.3 (3)
C4—C3—H3	119.4	N5—C15—H15	119.4
C2—C3—H3	119.4	C14—C15—H15	119.4
C3—C4—C5	118.4 (3)	O2—C16—N6	127.0 (4)
C3—C4—H4	120.8	O2—C16—C17	119.9 (3)
C5—C4—H4	120.8	N6—C16—C17	113.0 (3)
N1—C5—C4	121.9 (4)	N7—C17—C18	121.8 (4)
N1—C5—H5	119.1	N7—C17—C16	118.8 (3)
C4—C5—H5	119.1	C18—C17—C16	119.5 (3)
O1—C6—N2	127.6 (4)	N8—C18—C17	122.6 (4)
O1—C6—C7	119.8 (3)	N8—C18—H18	118.7
N2—C6—C7	112.6 (3)	C17—C18—H18	118.7
N3—C7—C8	122.4 (4)	N8—C19—C20	122.3 (4)
N3—C7—C6	117.9 (3)	N8—C19—H19	118.9

C8—C7—C6	119.7 (3)	C20—C19—H19	118.9
N4—C8—C7	122.2 (3)	N7—C20—C19	122.0 (4)
N4—C8—H8	118.9	N7—C20—H20	119.0
C7—C8—H8	118.9	C19—C20—H20	119.0
N4—C9—C10	122.2 (4)	C5—N1—C1	121.5 (3)
N4—C9—H9	118.9	C6—N2—C2	128.7 (3)
C10—C9—H9	118.9	C6—N2—H2	116 (3)
N3—C10—C9	122.4 (4)	C2—N2—H2	115 (3)
N3—C10—H10	118.8	C10—N3—C7	115.4 (3)
C9—C10—H10	118.8	C8—N4—C9	115.4 (3)
N5—C11—C12	119.8 (3)	C15—N5—C11	121.3 (3)
N5—C11—C11^{ii}	114.9 (4)	C16—N6—C12	129.0 (3)
C12—C11—C11^{ii}	125.2 (4)	C16—N6—H6	116 (3)
C13—C12—N6	121.9 (3)	C12—N6—H6	115 (3)
C13—C12—C11	118.3 (3)	C20—N7—C17	116.0 (3)
N6—C12—C11	119.8 (3)	C19—N8—C18	115.3 (4)

Symmetry code(s): (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*, −*z*+2.

S-2 $\{[Cu_6(L^3)_2(OAc)_6Cl_2]\cdot 2H_2O\cdot 2CH_3OH\}_n$, (1)

Bond Distances (Å)

Cu1-O1	1.968(12)	N1-C2	1.35(3)
Cu1-O2	1.953(11)	N2-C1	1.34(2)
Cu1-O3	1.951(11)	N2-C4	1.32(2)
Cu1-O4	1.967(13)	N3-C6	1.40(2)
Cu1-N1	2.195(14)	N3-C5	1.38(2)
Cu2-Cl1	2.398(6)	N4-C9	1.37(2)
Cu2-O6	1.941(13)	N4-C10	1.35(2)
Cu2-N2	2.151(15)	N5-C14	1.34(2)
Cu2-N3	1.923(16)	N5-C15	1.38(2)
Cu2-N4	2.077(13)	N6-C17	1.43(2)
Cu3 -Cl1	2.421(7)	N6-C18	1.33(2)
Cu3 -O7	1.927(13)	N7-C22	1.31(2)
Cu3 -N5	2.107(11)	N7-C19	1.36(2)
Cu3-N6	1.919(14)	N8-C21	1.29(3)
Cu3-N7	2.074(13)	N8-C20	1.36(3)
O1-C23	1.26(2)	C1-C2	1.40(3)
O2 -C25	1.23(2)	C3-C4	1.39(2)
O3 -C25^{ii}	1.255(19)	C4-C5	1.50(2)
O4 -C23^{ii}	1.24(2)	C6-C15^{i}	1.43(2)
O5 -C5	1.23(2)	C6-C7	1.38(2)
O6 -C12	1.27(2)	C7-C8	1.38(2)
O7-C12	1.26(2)	C8-C14^{i}	1.38(2)
O8 -C18	1.22(2)	C9-C15^{i}	1.48(2)
O10-C27	1.42(3)	C9-C17^{i}	1.39(2)
O10-H10S	0.8200	C10-C11	1.38(2)
O1S-H1S	1.0(6)	C11-C16^{i}	1.38(3)
O1S-H2S	1.0(3)	C12-C13	1.49(3)
N1-C3	1.32(2)	C16-C17	1.38(3)
C18-C19	1.50(2)	C14-H14	0.9300
C19-C20	1.39(3)	C16-H16	0.9300
C21-C22	1.38(3)	C20-H20	0.9300
C23-C24	1.53(3)	C21-H21	0.9300
C25-C26	1.49(3)	C22-H22	0.9300
C1-H1	0.9300	C24-H24B	0.9600
C2-H2	0.9300	C24-H24C	0.9600
C3-H3	0.9300	C24-H24A	0.9600
C7-H7	0.9300	C26-H26A	0.9600
C8-H8	0.9300	C26-H26B	0.9600
C10-H10	0.9300	C26-H26C	0.9600
C11-H11	0.9300	C27-H27C	0.9600
C13-H13C	0.9600	C27-H27A	0.9600
C13-H13B	0.9600	C27-H27B	0.9600
C13-H13A	0.9600		

Symmetry code(s): (i) = -x,2-y,-z; (ii) =1-x,1-y,1-z

Bond Angles (°)

O1-Cu1-O2	88.4(5)	N5 -Cu3 -N7	135.0(6)
O1-Cu1-O3	90.3(5)	N6-Cu3-N7	80.3(6)
O1-Cu1-O4	169.3(5)	Cu2-Cl1-Cu3	99.7(2)
O1-Cu1-N1	97.6(5)	Cu1-O1-C23	120.2(11)
O2-Cu1-O3	169.0(5)	Cu1 -O2 -C25	123.4(10)
O2-Cu1-O4	89.8(5)	Cu1-O3 -C25b	121.3(12)
O2-Cu1-N1	95.9(5)	Cu1 -O4 -C23b	124.0(13)
O3-Cu1-O4	89.5(5)	Cu2 -O6 -C12	139.6(11)
O3-Cu1-N1	95.2(5)	Cu3 -O7-C12	131.7(12)
O4 -Cu1-N1	93.2(5)	C27-O10 -H10S	110.00
Cl1-Cu2-O6	99.0(4)	H1S -O1S -H2S	111.00
Cl1-Cu2 -N2	102.4(4)	C2–N1-C3	116.8(15)
Cl1-Cu2 -N3	95.6(4)	Cu1-N1 -C3	121.3(13)
Cl1-Cu2 -N4	125.9(4)	Cu1-N1-C2	121.8(11)
O6-Cu2-N2	87.9(6)	Cu2-N2 -C1	131.5(14)
O6-Cu2-N3	163.0(6)	Cu2-N2-C4	109.8(11)
O6 -Cu2-N4	92.0(5)	C1-N2-C4	118.7(16)
N2-Cu2-N3	80.3(6)	Cu2-N3-C5	119.2(11)
N2-Cu2-N4	130.9(6)	C5 -N3-C6	118.1(15)
N3-Cu2 -N4	86.6(5)	Cu2 -N3-C6	121.4(12)
Cl1-Cu3 -O7	96.6(5)	C9 -N4 -C10	118.9(13)
Cl1-Cu3 -N5	105.5(4)	Cu2-N4 -C9	124.5(11)
Cl1-Cu3 -N6	94.8(5)	Cu2-N4-C10	114.3(11)
Cl1-Cu3 -N7	117.8(4)	C14-N5-C15	118.8(13)
O7-Cu3 -N5	98.3(5)	Cu3 -N5-C14	113.5(10)
O7-Cu3 -N6	167.0(6)	Cu3 -N5-C15	125.2(10)
O7-Cu3 -N7	88.7(6)	C17-N6-C18	119.6(15)
N5 -Cu3 -N6	84.8(5)	Cu3 -N6-C17	119.1(11)
Cu3 -N6 -C18	121.0(11)	N5-C15-C6^{i}	119.7(14)
C19-N7-C22	117.5(15)	N5-C15-C9^{i}	116.9(12)
Cu3-N7-C19	111.4(11)	C6a-C15 -C9^{i}	123.3(14)
Cu3-N7-C22	131.1(13)	C11a-C16 -C17	119.1(16)
C20-N8-C21	117.6(19)	C9a -C17-C16	121.0(17)
N2-C1-C2	120.5(19)	N6-C17-C9^{i}	119.8(15)
N1-C2-C1	121.0(17)	N6 -C17-C16	119.1(14)
N1-C3 -C4	122.8(18)	O8-C18-N6	129.5(16)
C3 -C4 -C5	121.0(17)	N6-C18-C19	111.0(15)
N2-C4-C3	120.2(16)	O8-C18-C19	119.6(16)
N2-C4-C5	118.8(15)	N7-C19-C18	116.0(15)
O5-C5-N3	129.1(16)	N7-C19-C20	120.1(16)
O5-C5-C4	119.8(15)	N8-C20-C19	120.6(18)
C7-C6 -C15^{i}	119.0(15)	N8-C21-C22	122(2)
N3-C6-C15^{i}	117.7(15)	N7-C22-C21	121.9(19)
N3 -C6 -C7	123.3(14)	O1-C23-O4b	126.5(18)
C6 -C7-C8	120.7(15)	O1-C23-C24	117.0(16)
C7-C8 -C14^{i}	118.1(17)	O4^{ii}-C23-C24	116.5(17)
N4 -C9-C17^{i}	119.4(15)	O2-C25-O3^{ii}	126.3(15)
N4-C9-C15^{i}	118.1(12)	O3^{ii}-C25-C26	115.9(17)
C15a -C9 -C17a	122.4(14)	O2-C25-C26	117.8(15)
N4-C10 -C11	123.2(17)	N2-C1-H1	120.00

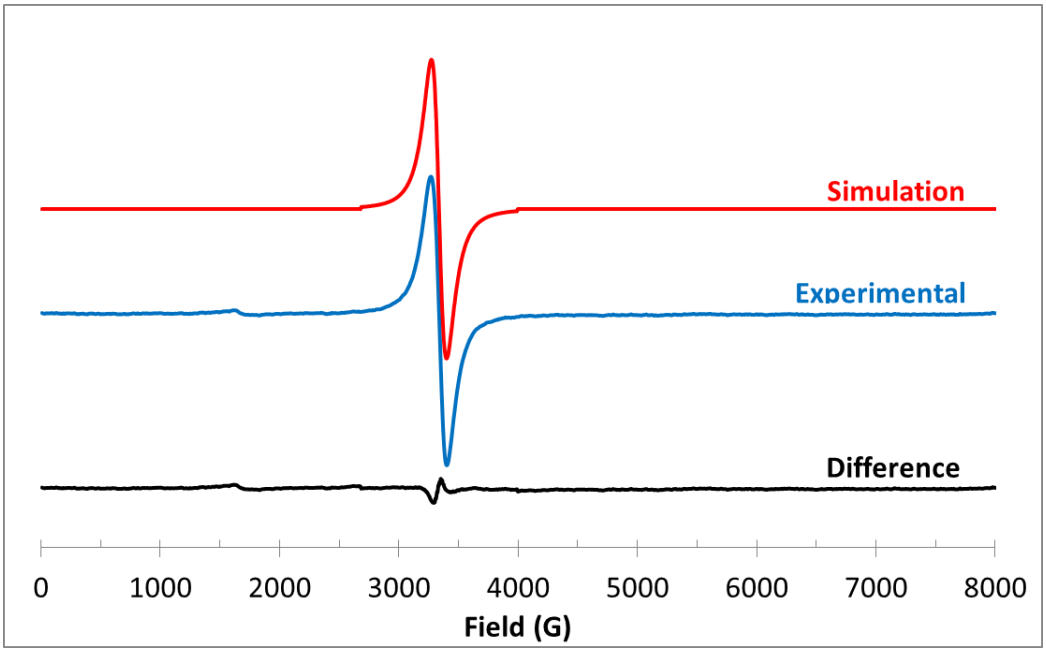
C10-C11 -C16^{i}	118.4(18)	C2-C1-H1	120.00
O6 -C12-C13	115.3(15)	N1-C2-H2	120.00
O6 -C12-O7	126.3(16)	C1-C2-H2	119.00
O7-C12-C13	118.3(17)	N1-C3-H3	119.00
N5-C14 -C8^{i}	123.7(16)	C4-C3-H3	119.00
C8 -C7-H7	120.00	C22-C21-H21	119.00
C6 -C7-H7	120.00	C21-C22-H22	119.00
C7-C8-H8	121.00	N7-C22-H22	119.00
C14a -C8 -H8	121.00	C23-C24 -H24A	109.00
N4-C10-H10	118.00	H24A-C24-H24B	109.00
C11-C10-H10	118.00	C23-C24-H24B	109.00
C16a -C11-H11	121.00	C23-C24-H24C	110.00
C10 -C11-H11	121.00	H24B-C24-H24C	109.00
C12-C13-H13C	109.00	H24A-C24-H24C	110.00
C12 -C13 -H13A	110.00	C25-C26-H26C	109.00
C12-C13-H13B	109.00	C25-C26-H26A	109.00
H13B-C13 -H13C	109.00	C25-C26-H26B	109.00
H13A -C13 -H13B	109.00	H26B-C26-H26C	110.00
H13A-C13-H13C	110.00	H26A-C26-H26B	109.00
N5-C14-H14	118.00	H26A-C26 -H26C	109.00
C8a -C14-H14	118.00	O10-C27-H27B	110.00
C11a-C16-H16	120.00	O10-C27-H27C	109.00
C17-C16-H16	121.00	O10-C27-H27A	109.00
N8 -C20 -H20	120.00	H27A-C27-H27C	109.00
C19 -C20-H20	120.00	H27V-C27-H27C	110.00
N8-C21-H21	119.00	H27A-C27-H27B	109.00

Symmetry code(s) (i) = -x,2-y,-z; (ii) =1-x,1-y,1-z

S-3 EPR Spectrum for (1)

Solid state room temperature EPR spectra of **1** were collected at room temperature on a Bruker EMX plus X-band EPR spectrometer between 0 and 8000 G (μ = 9.851 GHz with a modulation amplitude of 4 Gpp). Simulations were undertaken using PIP via a windows interface, PIP for Windows v1.2 to give g = 2.11 and a linewidth of 110 G (Lorentzian), Figure 1.

Figure 1. EPR spectrum for (**1**)



S-4 Bimetallic fragment geometries, energies and expectation values for (1).

Fragments of the polymeric structure of **1** were selected which reproduced the local coordination environment around the metal and the bridging ligands. Initial guesses of the broken symmetry singlet (ioss =1) and triplet configurations were defined using the &atomic command within Jaguar to define the formal charge (formal) and spin multiplicity (2spin) on each metal center and ligand. The LACV3P*+ basis set was employed which implemented triple-zeta 6-311G*+ for all non-metal atoms and an effective core potential LACV3P*+ for the Cu^{II} centers. The strength of the exchange interaction was determined using the method of Yamaguchi. However, particularly for the case of the paddlewheel dimer, the strength of magnetic communication was found to be particularly sensitive to the functional employed and the functional chosen; B3LYP over-estimated the value of ***J*** by two orders of magnitude, whereas PBE0 over-estimated ***J*** by one order of magnitude. Whilst the Minnesota functional M06-L also over-estimated ***J***, the value was the correct order of magnitude and used for subsequent discussion. Whilst there is considerable uncertainty in the computed energies of the exchange interactions we see that exchange within the paddlewheel is significantly larger than exchange within the tetrameric unit. Moreover at all levels of theory implemented the exchange via the acetato-/chloro-bridge is ferromagnetic whereas it is antiferromagnetic through the bipy ligand.

Paddlewheel fragment (symmetry C_1 ,748 basis functions)

B3LYP/LACV3P*+

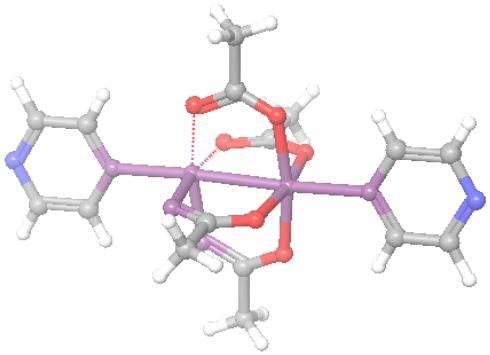
E(T)/Hartree	-1835.1319727978
E(BSS)/Hartree	-1835.19090899742
$<S^2_T>$	2.020
$<S^2_{BSS}>$	0.985
J/*k*	-17,856 K

PBE0/LACV3P*+

E(T)/Hartree	-1833.31178125393
E(BSS)/Hartree	-1833.32094955132
$<S^2_T>$	2.028
$<S^2_{BSS}>$	1.018
J/*k*	-2,847 K

M06-L/LACV3P*+

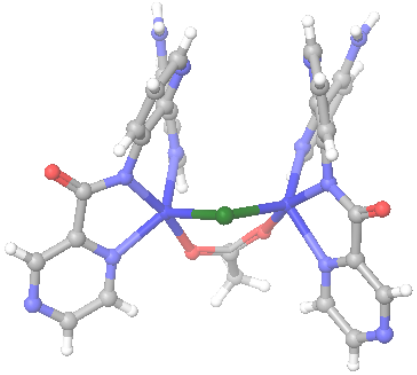
E(T)/Hartree	-1835.07267269736
E(BSS)/Hartree	-1835.07505748497
$<S^2_T>$	2.004
$<S^2_{BSS}>$	0.936
J/*k* /K	-700 K



Chloro-/acetate bridged fragment (symmetry C_1, 1233 basis functions)

B3LYP/LACV3P*+

E(T)/Hartree	-3045.23776319708
E(BSS)/Hartree	-3045.23768193723
$<S^2_T>$	2.006
$<S^2_{BSS}>$	1.006
J/*k*	+25 K



PBE0/LACV3P*+

E(T)/Hartree	-3042.41924553287
E(BSS)/Hartree	-3042.4191783422
$<S^2_T>$	2.007
$<S^2_{BSS}>$	1.007
J/*k*	+21 K

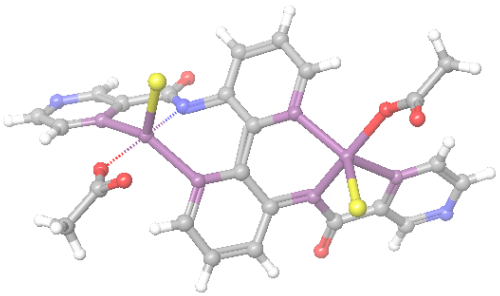
M06-L/LACV3P*+

E(T)/Hartree	-3045.02967338554
E(BSS)/Hartree	-3045.02953656072
$<S^2_T>$	2.007
$<S^2_{BSS}>$	1.000
J/*k* /K	+43 K

Bipyridine-bridged fragment (symmetry C_1 , 1022 basis functions)

B3LYP/LACV3P*+

E(T)/Hartree	-3127.96974834258
E(BSS)/Hartree	-3127.96975794761
$<S^2_T>$	2.007
$<S^2_{BSS}>$	1.008
J/*k*	-3 K



PBE0/LACV3P*+

E(T)/Hartree	-3125.42853482282
E(BSS)/Hartree	-3125.42854793492
$<S^2_T>$	2.007
$<S^2_{BSS}>$	1.008
J/*k*	-4 K

M06-L/LACV3P*+

E(T)/Hartree	-3127.77864359824
E(BSS)/Hartree	-3127.7786543106
$<S^2_T>$	2.010
$<S^2_{BSS}>$	1.011
J/*k* /K	-3 K