Supplementary Materials

An N4-tetradentate hydrazone ligand that binds in a neutral, mono- and bisdeprotonated form to iron(II) and zinc(II) metal ions

Devaraj Pandiarajan, Thomas Fox and Bernhard Spingler*

University of Zürich, Department of Chemistry, Winterthurerstr. 190, CH-8057 Zürich, Switzerland.

Fax: +41 44 635 68 02; E-mail: spingler@chem.uzh.ch.

Contents **Pages**

Figure S1: ^{1}H-NMR spectrum of **3** S2

Figure S2: ^{1}H-NMR spectrum of **4** S3

Figure S3: Crystal structure of complex **5** (Asymmetric unit) S4

Table S1: Crystallographic Information S5 – S6

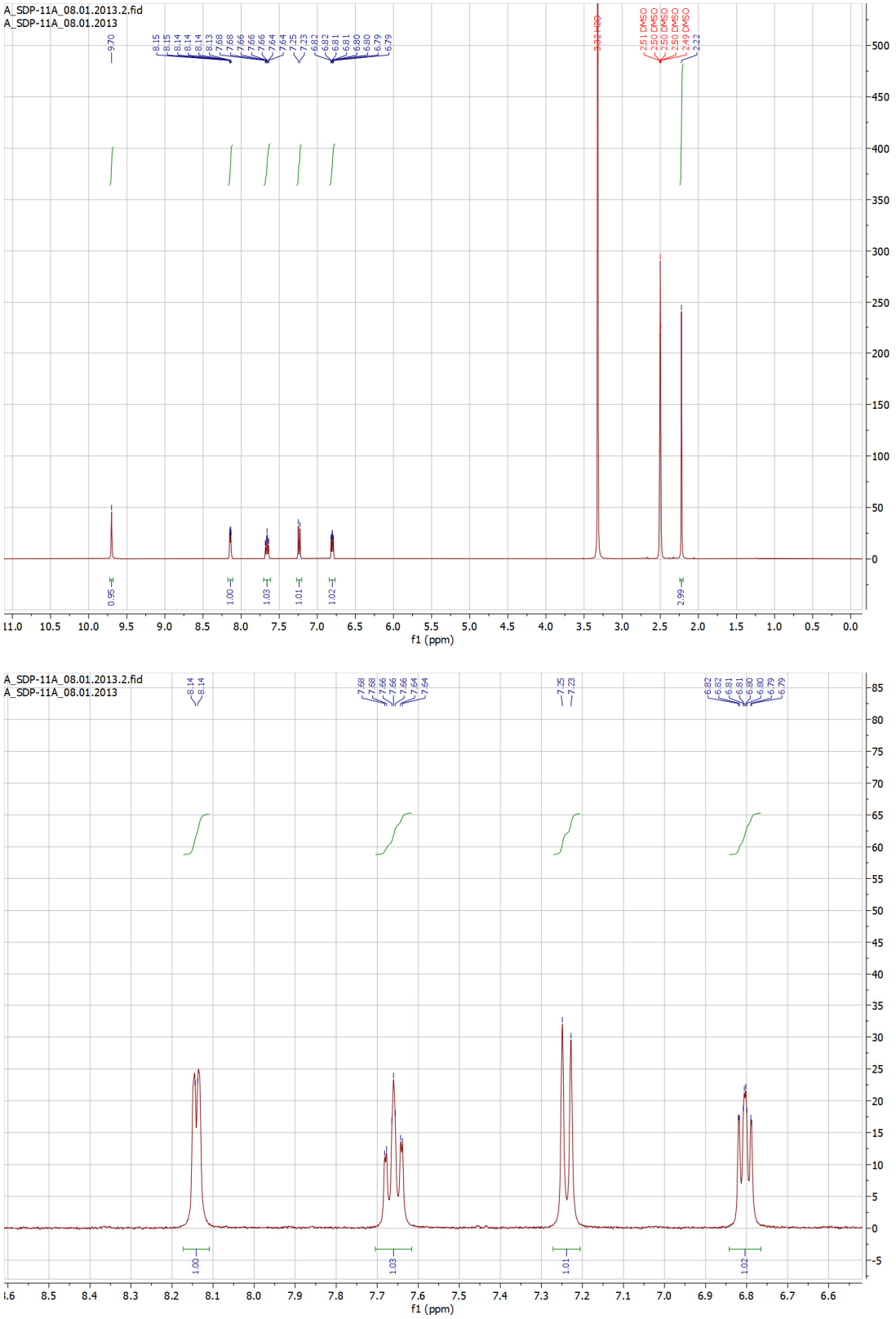

Figure S1. ^{1}H-NMR spectrum of complex **3** in $D_3CS(O)CD_3$ including enlargement of aromatic region.

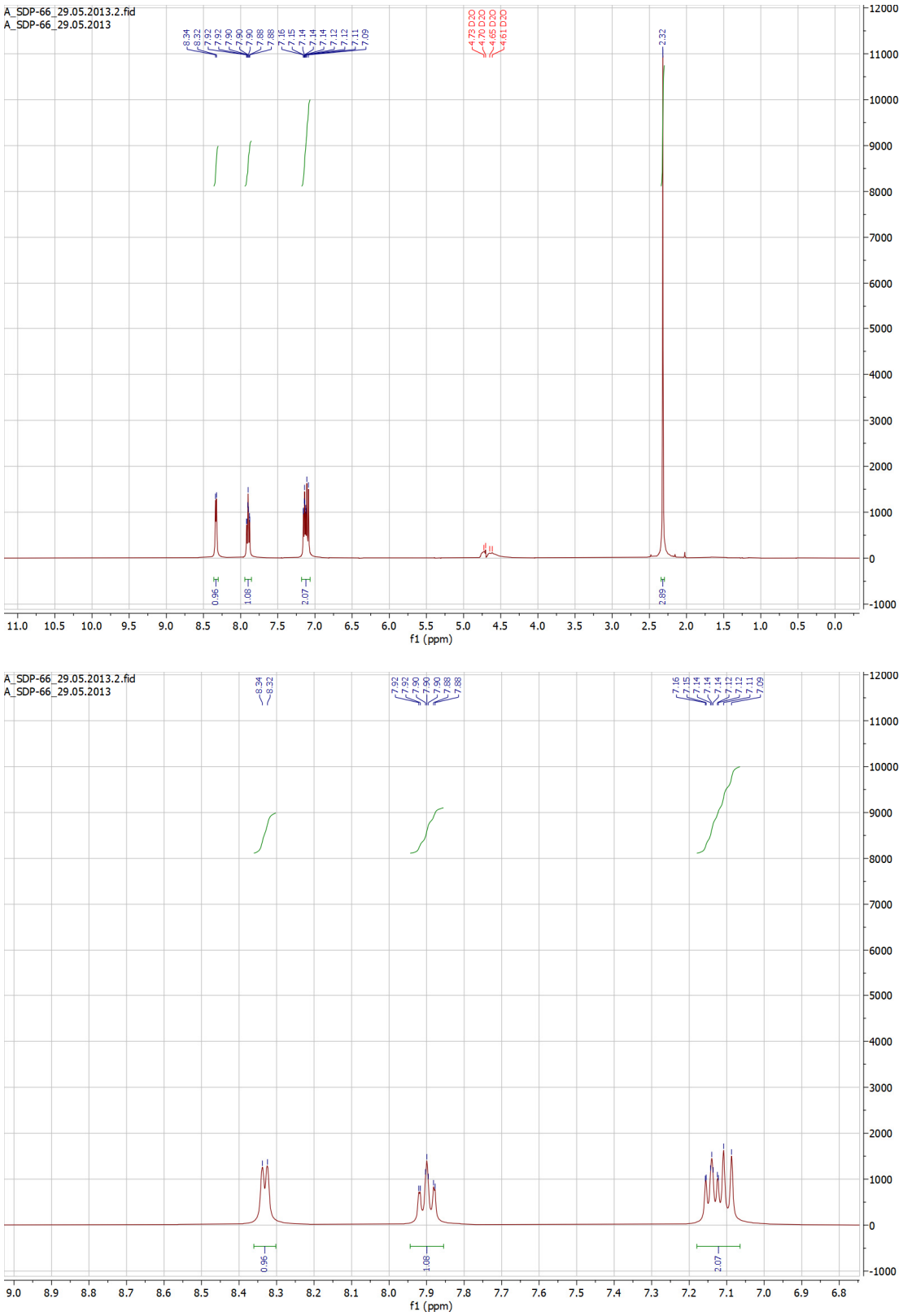

Figure S2. ^{1}H-NMR spectrum of complex **4** in D_2O including enlargement of aromatic region.

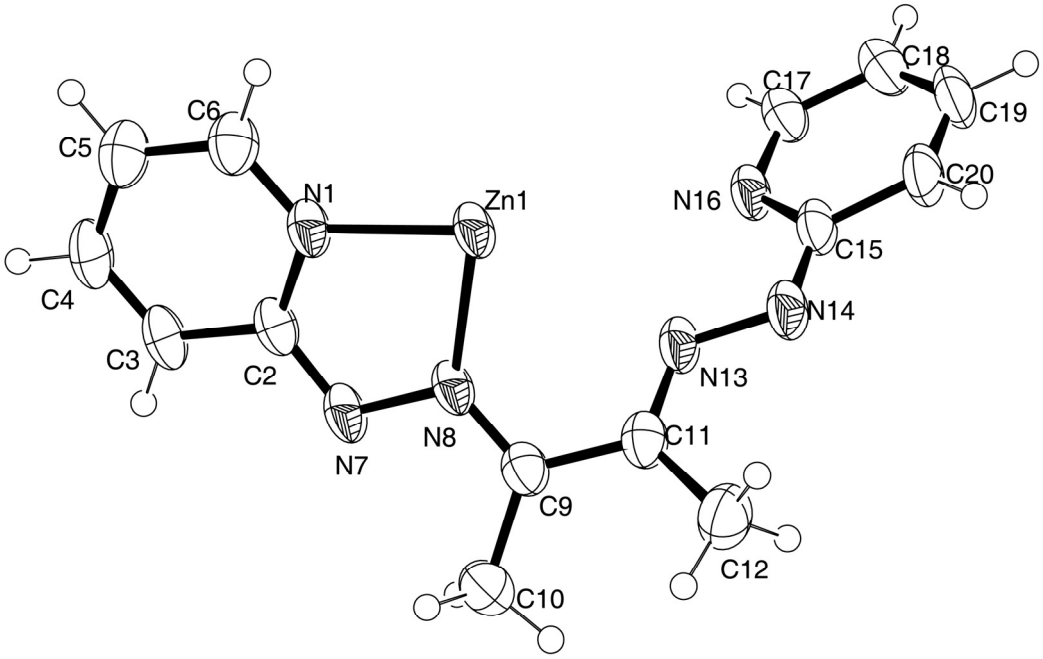

Figure S3. ORTEP representation of an asymmetric unit of the Zn-Zn dimer (**5**)

Table S1. Crystal data and structure refinement parameters for complexes **1**-**6**

Compounds	$[Zn(LH_2)Cl_2]$ (**1**)	$[Zn(LH_2)(OAc)_2]\cdot H_2O$ (**2**)	$[Zn(LH_2)(N_3)_2]$ (**3**)
Empirical formula	$C_{14}H_{16}Cl_2N_6Zn$	$C_{18}H_{24}N_6O_5Zn$	$C_{14}H_{16}N_{12}Zn$
Formula weight	404.60	469.80	417.76
Wavelength [Å]	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 1 2/n 1	P 1 21/c 1	P-1
a [Å]	8.4935(5)	8.57160(14)	8.0537(2)
b [Å]	9.7578(6)	14.6873(2)	9.5480(3)
c [Å]	9.8536(6)	16.3014(2)	11.6897(3)
α [°]	90	90	81.461(2)
β [°]	100.795(6)	91.1754(13)	88.337(2)
γ [°]	90	90	77.855(3)
Volume [$Å^3$]	802.19(9)	2051.81(5)	869.04(4)
Z	2	4	2
Density (calculated) [Mg/m^3]	1.675	1.521	1.596
Absorption coefficient [mm^{-1}]	1.871	2.043	2.217
F(000)	412	976	428
Crystal size [mm^3]	0.22 x 0.17 x 0.04	0.12 x 0.1 x 0.06	0.16 x 0.05 x 0.04
Crystal description	light yellow plate	colorless prism	yellow needle
Theta range for data collection [°]	2.964 to 32.808	4.052 to 74.290	3.824 to 74.452
Index ranges	-8<=h<=12, -13<=k<=13, -11<=l<=14	-10<=h<=8, -18<=k<=18, -20<=l<=19	-10<=h<=10, -11<=k<=11, -14<=l<=14
Reflections collected	5658	12158	29633
Independent reflections	2654 [R(int) = 0.0504]	4061 [R(int) = 0.0191]	3275 [R(int) = 0.0376]
Reflections observed	2179	3601	3007
Completeness to theta	99.9 % to 25.242°	99.6 % to 67.684°	94.5 % to 67.684°
Max. and min. transmission	1.00000 and 0.82475	1.00000 and 0.90121	1.00000 and 0.79120
Data / restraints / parameters	2654 / 0 / 106	4061 / 2 / 281	3275 / 0 / 246
Goodness-of-fit on F^2	1.027	1.116	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1003	R1 = 0.0377, wR2 = 0.0990	R1 = 0.0415, wR2 = 0.1204
R indices (all data)	R1 = 0.0593, wR2 = 0.1076	R1 = 0.0448, wR2 = 0.1020	R1 = 0.0450, wR2 = 0.1250
Largest diff. peak and hole [$e.Å^{-3}$]	0.930 and -0.552	0.459 and -0.525	0.957 and -0.735
CCDC number	1017003	1017004	1017005

Compounds	$[Zn(LH_2)OTf_2]$ (**4**)	$[Zn_2(L)_2]$ (**5**)	$[Fe(LH)_2]\cdot H_2O$ (**6**)
Empirical formula	$C_{16}H_{16}F_6N_6O_6S_2Zn$	$C_{28}H_{28}N_{12}Zn_2$	$C_{28}H_{32}FeN_{12}O$
Formula weight	631.84	663.36	608.50
Wavelength [Å]	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	I2/a	P-1
a [Å]	14.6922(4)	15.3105(7)	8.2454(2)
b [Å]	10.5125(2)	12.1441(5)	11.0379(2)
c [Å]	17.3013(5)	15.6339(6)	16.9513(4)
α [°]	90	90	97.230(2)
β [°]	120.944(4)	92.310(4)	93.365(2)
γ [°]	90	90	110.444(2)
Volume [$Å^3$]	2291.88(13)	2904.5(2)	1425.33(6)
Z	4	4	2
Density (calculated) [Mg/m^3]	1.831	1.517	1.418
Absorption coefficient [mm^{-1}]	4.106	2.368	4.619
F(000)	1272	1360	636
Crystal size [mm^3]	0.13 x 0.1 x 0.06	0.13 x 0.11 x 0.07	0.35 x 0.2 x 0.1
Crystal description	yellow plate	red prism	dark brown plate
Theta range for data collection [°]	5.306 to 76.109	4.612 to 75.928	2.644 to 76.166
Index ranges	-18<=h<=18, -10<=k<=12, -21<=l<=21	-14<=h<=17, -15<=k<=15, -19<=l<=19	-10<=h<=10, -13<=k<=13, -20<=l<=19
Reflections collected	13446	12417	25820
Independent reflections	2320 [R(int) = 0.0189]	2945 [R(int) = 0.0379]	5513 [R(int) = 0.0457]
Reflections observed	2250	2702	4697
Completeness to theta	97.9 % to 67.684°	98.6 % to 67.684°	94.8 % to 67.684°
Max. and min. transmission	1.00000 and 0.83624	1.00000 and 0.68734	1.00000 and 0.55870
Data / restraints / parameters	2320 / 0 / 169	2945 / 0 / 192	5513 / 2 / 395
Goodness-of-fit on F^2	1.066	1.119	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0867	R1 = 0.0633, wR2 = 0.1761	R1 = 0.0485, wR2 = 0.1271
R indices (all data)	R1 = 0.0318, wR2 = 0.0871	R1 = 0.0661, wR2 = 0.1802	R1 = 0.0598, wR2 = 0.1352
Largest diff. peak and hole [$e.Å^{-3}$]	0.681 and -0.462	2.720 and -1.137	0.420 and -0.467
CCDC number	1017006	1017007	1017008