Supporting Information

to the manuscript

Unique Molecular Geometries of Reduced 4- and 5-Coordinate Zinc Complexes Stabilised by Diiminopyridine Ligand

by

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Materials and Methods

All manipulations were performed using standard inert atmosphere (N_2 gas) glovebox and Schlenk techniques. Benzene, toluene, and hexanes were dried and purified using a Grubbs-type solvent purification system. The deuterated solvents d_6-benzene and d_8-toluene were predried and distilled from K/Na alloy and stored in a glass vessel in the glovebox. NMR spectra were obtained with a Bruker AVANCE III HD 400 MHz and AVANCE I 600 MHz spectrometers (^{1}H, 400 and 600 MHz; ^{13}C, 101 and 151 MHz) at room temperature, unless stated otherwise, then processed and analyzed with MestReNova software (v10.0.2-15465). IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed by the ANALEST laboratory at the University of Toronto. 4-dimethylaminopyridine (DMAP) was purchased from Sigma-Aldrich and sublimed before use. The diimino pyridine ligand[1] and compound **1**[2] were prepared according to literature procedures.

EPR Spectroscopy

EPR spectra were collected on a Bruker Elexys E580 instrument operating in continuous wave mode. The spectra shown in Figure 1 were collected under the following conditions: microwave frequency 9.843 GHz, microwave power 0.63 mW, modulation amplitude 0.03 mT. The simulation of the EPR spectra was carried out using Easyspin.[3] The motion was assumed to be in the isotropic limit. The hyperfine couplings used in the simulation are given in Table 1, the inhomogeneous Gaussian linewidths are reported in the caption to Figure 1 and the g-value obtained from the simulations is g=1.999.

X-ray Crystallography

Data collection results for compounds **2**–**5** represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fiber using paraffin oil. Prior to data collection crystals were cooled to 200 K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.[4] Diffraction data for all four samples were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[5] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic **P***2$_1$/n* (№14) for compounds **2** and **4** and triclinic **P**-*1* (№2) for compounds **3** and **5**. Solutions in the centrosymmetric space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2.

Refinement results for the compounds **3** and **5** suggested the presence of two non-merohedrally twinned domains in both cases. Careful examination of the original data frames and reciprocal space diffraction pictures for both samples confirmed the initial twining assumption. In order to find independent orientation matrices for each sample, a number of independent reflections (1337 and 3258 reflections for compounds **3** and **5**, respectively) were collected from 4 independent sets of 40 frames in the different sections of the Ewald sphere. Collected reflection data were processed with CELL_NOW software[6] and produced two independent orientation matrices in each case. Both data sets were re-integrated using obtained

matrices, treated for twinning absorption corrections and consecutive structural models refinement was performed using HKLF5 reflection data files. The twinning domain ratio coefficient (BASF) was refined to 0.31708 and 0.23463 for compound **3** and **5**, respectively.

All structural models were refined with full set of anisotropic thermal displacement coefficient for all non-hydrogen atoms. For all compounds all hydrogen atom positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.[7]

Table SI1.

Crystal and structure refinement data for compounds **2**, **3**, **4**, and **5**.

	2	**3**	**4**	**5**
Empirical formula	$C_{33}H_{43}ClN_3Zn$	$C_{40}H_{53}ClN_5Zn$	$C_{34}H_{46}N_3Zn$	$C_{20}H_{20}N_3Zn$
Formula weight	582.52	704.69	562.11	367.76
Crystal habit	block	block	block	block
Crystal colour	green	red	red	green
Temperature, K	200(2)	200(2)	200(2)	200(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	P-1	$P2_1/n$	P-1
Unit cell dimensions:				
a, Å	8.6852(2)	8.8613(4)	14.328(2)	14.5172(4)
b, Å	13.9641(4)	12.6319(6)	8.7698(13)	18.2605(5)
c, Å	25.8243(7)	17.9583(8)	25.005(4)	19.9983(5)
α, °	90	108.539(2)	90	90.5750(17)
β, °	92.0765(12)	90.012(2)	93.489(7)	109.8856(15)
γ °	90	93.205(2)	90	97.8222(16)
Volume, $Å^3$	3129.94(14)	1905.28(15)	3136.3(8)	4929.8(2)
Z	4	2	4	12
Density (calc), Mg/m^3	1.236	1.228	1.190	1.486
Absorption coeff., mm^{-1}	0.895	0.748	0.808	1.500
F(000)	1236	750	1204	2292
Crystal size, mm^3	0.13 x 0.11 x 0.10	0.19 x 0.12 x 0.10	0.20 x 0.16 x 0.12	0.24x 0.21 x 0.21
θ range for data collection	1.578 to 28.245	1.741 to 28.349	1.579 to 28.338	1.988 to 30.555

Index ranges	-11<=h<=10, -17<=k<=18, -27<=l<=30	-11<=h<=11, -16<=k<=15, 0<=l<=23	-19<=h<=19, 0<=k<=11, 0<=l<=33	-20<=h<=19, -25<=k<=25, 0<=l<=28
Reflections collected	30834	28106	11644	40318
Independent reflections	6787 [R(int) = 0.0427]	28106 [R(int) = 0.0292]	11644 [R(int) = 0.0499]	27446 [R(int) = 0.0482]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6493	0.745685 and 0.649428	0.745686 and 0.601014	0.746068 and 0.651904
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6787 / 0 / 343	9342/ 21 / 425	5714 / 0 / 354	27446 / 85 / 1109
Goodness-of-fit on F^2	1.025	0.863	1.073	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0937	R1 = 0.0465, wR2 = 0.1223	R1 = 0.0591, wR2 = 0.1723	R1 = 0.0697, wR2 = 0.1682
R indices (all data)	R1 = 0.0671, wR2 = 0.1048	R1 = 0.0676, wR2 = 0.1397	R1 = 0.0703, wR2 = 0.1768	R1 = 0.1519, wR2 = 0.2078
Largest diff. peak and hole, e.$Å^{-3}$	0.730 and -0.391	0.543 and -0.625	0.843 and -0.424	0.736 and -1.020

DFT Computational Details

Calculations were carried out at the Kohn-Sham hybrid-DFT uwB97XD[8,9]/6-31+G(d,p) level of theory using the Gaussian 09[10] and GaussView v5.0.8 programs. Input geometries were obtained from the atomic coordinates of the X-ray crystal structures.

Calculated Atomic Coordinates and Energies

dimpyrZnCl (**2**)

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uwb97xd/6-31+g(d,p)/def2sv

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0 2

Zn	-0.39280700	-0.54089500	-0.05338700
Cl	-0.17178200	-1.32931000	-2.13660900
N	-0.29542200	-1.10209500	1.87795500
N	1.99290700	-1.10092100	0.54086100
N	-2.39386900	-0.44919200	0.44082600
N	0.13375300	1.43248600	-0.17615800
N	1.59754700	5.33835500	-0.37212300
C	3.31249000	-2.02086900	2.42605600
H	4.14459100	-2.07220500	1.72492400
H	3.11986500	-3.01823000	2.82994800
H	3.60041800	-1.38303600	3.26726000
C	2.07297000	-1.47945100	1.76026900
C	0.82055500	-1.41070100	2.56902500
C	0.80682000	-1.67400700	3.92054300
H	1.71602600	-1.92117400	4.45258200
C	-0.43387700	-1.61987100	4.60875200
H	-0.47340000	-1.82259400	5.67362200
C	-1.57411800	-1.31610000	3.91764300
H	-2.52950600	-1.27491900	4.42859500
C	-1.51239600	-1.04589800	2.52548100
C	-2.63677800	-0.71217600	1.72125900
C	-4.01334800	-0.67111800	2.33148200
H	-4.76980400	-0.48896400	1.56733300
H	-4.08976600	0.12356000	3.08224700
H	-4.25257600	-1.61622500	2.82970400
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C	3.95881200	-0.14877700	-0.56459200
C	3.72096400	1.19387200	0.11276300
H	2.64452300	1.28065500	0.28209500
C	0.22177300	2.19640000	0.92032300
H	-0.08205400	1.72547600	1.85137000
C	0.68431300	3.49400800	0.91088500
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C	1.08991800	4.07635300	-0.31120100
C	0.96037800	3.27109800	-1.46364800
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C	4.38668000	-2.59433300	-1.85229100
H	4.55092500	-3.53645300	-2.36623700
C	5.27158400	-1.54545000	-2.05100100
H	6.12505000	-1.66722700	-2.71040400
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C	2.32804300	-3.63929700	-0.83258900
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C	1.88933400	-4.23324600	-2.17631100
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H	4.04466200	0.51801900	2.16902200
H	4.23117900	2.25951900	1.93926700
H	5.49346800	1.14727500	1.37472400
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H	3.80491900	3.31777300	-0.29649800
H	3.72679200	2.31716200	-1.75896500
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H	-5.29111200	2.52496200	-1.52738200
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H	-6.21002200	0.78017100	-3.01116500
C	-3.28530300	-3.23056900	-2.56215700
H	-2.65809000	-2.62886000	-3.22347100
H	-4.24971900	-3.41121000	-3.05068100
H	-2.80050400	-4.20284300	-2.42949800
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H	-1.99974700	3.07527100	-1.15917600
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H	-4.87697400	2.05094700	1.91487900
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C	1.73278100	6.12329300	0.83943000
H	0.76299700	6.27555000	1.32699600
H	2.13810900	7.10317400	0.59008300
H	2.41249300	5.64807100	1.55812900
C	2.09063400	5.85813400	-1.63411200
H	1.28893500	5.94356700	-2.37680200
H	2.88117600	5.21966400	-2.04663900

H	2.50873500	6.85130400	-1.47459800	H	3.23771900	-4.34678400	1.03411400
C	2.94177700	-4.73124100	0.05526600	H	3.83496300	-5.15660700	-0.41588700
H	2.22490300	-5.54368100	0.21165800				

dimpyrZnCl(DMAP) (**3**)

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uwb97xd/6-31+g(d,p)/def2sv

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N	0.03164900	-1.63141600	-1.18491600	N	2.06362400	-0.25513900	-0.40367500
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C	-1.13015300	-2.07355700	-1.70939600	C	1.25140900	-2.94865600	-2.77269400
C	-1.16425200	-3.01199700	-2.71129100	H	2.19613300	-3.26905100	-3.19782300
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C	0.07122700	-3.48747700	-3.22576000	C	3.73191800	-1.46480400	-1.81193500
H	0.07765000	-4.24544800	-4.00079900	H	4.39856700	-0.63657400	-1.56801400
C	-2.32764700	-1.40156900	-1.14516400	H	3.73059600	-1.59946500	-2.89697900
C	-3.69283400	-1.84183300	-1.58773900	H	4.15093500	-2.37276300	-1.36333700
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H	-3.81506200	-2.91784900	-1.43785400	C	3.12434400	1.90737000	-0.15511300
H	-3.81479600	-1.64120900	-2.65698100	C	4.10671100	2.70528900	0.42516000
C	-3.15436300	0.29274500	0.27722400	H	4.16229700	3.75930000	0.17400600
C	-3.67543800	-0.14740400	1.50165500	C	5.01184500	2.17468300	1.33600600
C	-4.70113900	0.60395700	2.07803500	H	5.77127000	2.81001200	1.78065600
H	-5.13241000	0.27717800	3.01917500	C	4.92485900	0.83772400	1.69396000
C	-5.17617100	1.75733500	1.47391200	H	5.61133900	0.43835100	2.43495500
H	-5.97430000	2.32626300	1.93977100	C	3.95946700	-0.00084100	1.13518400
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C	-3.60365400	1.47150200	-0.34498600	C	2.54311900	2.20840400	-2.58852900
C	-3.17638700	-1.41215500	2.18339600	H	2.68623300	1.14004100	-2.77208700
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H	-2.39845000	-2.08383000	4.08910300	H	3.13395300	-1.95943800	0.96315100
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C	-2.93931400	1.95340600	-1.62550700	H	5.62767800	-2.14545200	0.62198600
H	-2.69546100	1.07013100	-2.22729600	H	4.98949900	-3.24916300	1.85607400
C	-3.82615100	2.85186300	-2.48939900	H	5.86143800	-1.79406400	2.33831400
H	-4.79544100	2.38606400	-2.69016000	C	3.19342000	-1.44640800	3.02838300
H	-3.33570800	3.04841700	-3.44730100	H	2.22919300	-0.93005200	3.02635000
H	-4.00566500	3.82131400	-2.01335400	H	3.84413500	-0.94064600	3.74996800
C	-1.61738400	2.65951300	-1.29003700	H	3.04107700	-2.47503000	3.37255800
H	-0.98947200	2.03893300	-0.64554200	Zn	0.09962800	-0.19872800	0.15824200
H	-1.80507000	3.59056600	-0.74639500	Cl	-0.06361500	0.75515500	2.11351300

dimpyrZn(DMAP)$_2$ (**5**)

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uwb97xd/6-31+g(d,p)/def2sv

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0 1

Zn	-0.43385100	-0.45192100	-0.43062400	C	-5.41942100	0.62219600	-0.07896800
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N	-2.26715400	-1.30779200	-0.46661400	H	-6.56767200	0.66537500	1.56666500
N	0.93067300	-1.61793700	0.72702100	C	-4.98375500	-0.56588800	1.93215700
N	-0.42537100	1.14747900	0.88598400	H	-5.22780700	-0.76871600	2.82760000
N	3.62314200	-4.10507800	2.74965700	C	-3.84250600	-1.13911300	1.39056000
N	-0.17804000	3.89921700	4.04156300	C	-3.85693400	0.54140000	-2.05649400
C	2.59843000	0.33654900	-3.96415200	H	-3.18622200	-0.11703700	-2.39797100
H	3.14387000	1.09214100	-3.66083500	C	-3.16445900	1.89311500	-1.98225600
H	2.11592500	0.58831800	-4.77912300	H	-2.90046100	2.17480100	-2.88301000
H	3.17862200	-0.43061400	-4.15182800	H	-2.36796500	1.82144900	-1.41583100
C	1.61540600	-0.03057300	-2.89514600	H	-3.77867200	2.55425800	-1.60012100
C	0.69494900	-1.15268100	-3.13547900	C	-4.99712000	0.58205800	-3.05666900
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H	-0.03336800	-3.66566100	-5.09407000	C	-3.00979200	-2.10095000	2.20954200
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C	-1.31110600	-2.25451400	-2.41442200	H	-1.97961600	-0.63657300	3.22487300
C	-2.36306700	-2.20233500	-1.52354100	H	-1.86263300	-2.07410600	3.91830400
C	-3.56083300	-3.08294000	-1.64697800	H	-3.21116700	-1.22427900	4.06087100
H	-3.47112000	-3.64671900	-2.44353400	C	-3.77913200	-3.39006000	2.54739500
H	-4.36595500	-2.53001500	-1.72708800	H	-4.11508500	-3.79603900	1.72113800
H	-3.63226100	-3.65064900	-0.85135300	H	-4.53280600	-3.17593500	3.13606400
C	2.32956900	1.73226000	-1.50564500	H	-3.17948000	-4.01920800	3.00015400
C	1.78636600	3.01824200	-1.62904800	C	1.03898700	-1.59458600	2.05424400
C	2.58045900	4.12090100	-1.28377300	H	0.48969300	-0.98959700	2.53878000
H	2.23711000	5.00096700	-1.38433500	C	1.90997800	-2.40525700	2.76845300
C	3.86583400	3.93240000	-0.79577100	H	1.94174100	-2.35210200	3.71643300
H	4.38895100	4.68344800	-0.54124800	C	2.73583900	-3.29541900	2.09156700
C	4.38321000	2.67458800	-0.67921000	C	2.62570000	-3.32272700	0.68898700
H	5.26471000	2.56121800	-0.34367600	H	3.16390800	-3.91209000	0.17373600
C	3.63886400	1.55322700	-1.04463600	C	1.73012100	-2.48590400	0.07928700
C	0.37629900	3.22399700	-2.13579000	H	1.66847000	-2.52015900	-0.86808900
H	-0.08678600	2.34053000	-2.06490800	C	4.44555300	-5.05764400	1.98932300
C	0.36497500	3.60267900	-3.58950600	H	4.24325000	-4.97404100	1.03407800
H	0.88032700	2.94551700	-4.10229500	H	4.24737200	-5.97020600	2.28654700
H	0.76629000	4.49003500	-3.69906000	H	5.39414900	-4.86359300	2.14054700
H	-0.55905200	3.61957500	-3.91549200	C	3.75012200	-4.05341600	4.15543600
C	-0.41968100	4.20551700	-1.28603200	H	3.13959300	-3.37580500	4.51390400
H	-1.32479600	4.29437900	-1.65110000	H	4.67214200	-3.82014000	4.39180900
H	0.02345500	5.07956000	-1.29505800	H	3.52675300	-4.92845900	4.53599100
H	-0.46996300	3.87425200	-0.36508200	C	0.75225900	1.65084800	1.32634900
C	4.24256800	0.16525100	-0.86048000	H	1.54452800	1.34941300	0.89744100
H	3.59215900	-0.50663200	-1.21480600	C	0.89135800	2.55955300	2.34056300
C	5.53155200	0.03742200	-1.65101400	H	1.75199300	2.87907800	2.58484800
H	5.35523300	0.22680200	-2.59621900	C	-0.25539400	3.01481600	3.01705500
H	5.88154600	-0.87343100	-1.56012300	C	-1.47888100	2.50107000	2.55925300
H	6.19035600	0.67631400	-1.30720900	H	-2.29015200	2.77108300	2.97332100
C	4.49715200	-0.14974200	0.60613400	C	-1.50731100	1.61289600	1.51894800
H	3.66174100	-0.05693200	1.10999400	H	-2.35660400	1.30479300	1.22525700
H	5.16467700	0.47282600	0.96285900	C	1.10757400	4.41962100	4.47020100
H	4.82903000	-1.06799300	0.69021100	H	1.80359500	4.12534500	3.84622400
C	-3.47334600	-0.81368500	0.07814300	H	1.31199800	4.08584300	5.36867700
C	-4.26768000	0.08627900	-0.66555900	H	1.07503700	5.39895500	4.48509800

C	-1.31440900	4.24351900	4.87316000
H	-2.12785200	3.84986100	4.49403500
H	-1.40937000	5.21824600	4.90924100
H	-1.17421200	3.89523800	5.77840300

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