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Zn-bisSalen MOFs

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Catalytic Transesterifications by a Zn-BisSalen MOF Containing Open Pyridyl Groups Inside 1D Channels

Keywords: Metal–organic frameworks / Salen ligands / Heterogeneous catalysis / Metalloligands / Transesterification



A 3D-like 2D Zn-bisSalen MOF {bisSalen = N,N',N'',N'''-tetrakis[3-*tert*-buty]-5-(4pyridinyl)salicylidene]-1,2,4,5-benzenetetraamine} with a large void space and Lewis-basic openly accessible pyridyl groups inside 1D channels was prepared and structurally investigated. The solventfree Zn-bisSalen MOF contains a solventaccessible void volume of 41.1%. The asprepared Zn-bisSalen MOF effectively catalyzes transesterifications.



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Catalytic Transesterifications by a Zn–BisSalen MOF Containing Open Pyridyl Groups Inside 1D Channels

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Keywords: Metal-organic frameworks / Salen ligands / Heterogeneous catalysis / Metalloligands / Transesterification

The new ligand N,N',N''-tetrakis[3-tert-butyl-5-(4-pyridinyl)salicylidene]-1,2,4,5-benzenetetraamine (bisSalen) containing four pyridyl groups in its periphery was prepared and subsequently used as an organic linker for a Zn-bisSalen MOF. A 2D undulated sheet structure was determined from single-crystal X-ray diffraction studies. The bisSalen ligands bridge two Zn^{II} ions, and one of the pyridyl groups on each side of the bisSalen ligand further coordinates to a bisSalencoordinated Zn^{II} ion to provide a 2D sheet structure. The un-

Introduction

Currently, many research efforts are aiming for the preparation and utilization of functional metal–organic frameworks (MOFs).^[1] Applications in catalysis^[2] as well as in gas sorption^[3] and separation^[4] make MOF systems a unique class of crystalline, porous materials. Particularly for catalysis applications, several strategies to prepare novel MOF-based catalysts are being employed. The use of Lewis-acidic metal ions as catalytic centers may be the most popular approach.^[5] There are many previous examples for the utilization of Lewis-acidic catalytic centers. However, a prerequisite of this type of MOF-based catalytic systems is the presence of well-defined coordinatively unsaturated openly accessible metal sites.^[6] Otherwise, the catalytic reactions mainly occur on the surfaces of MOFs, which may

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dulated 2D sheets are stacked closely together to form a 3Dlike structure containing well-defined 1D channels, the orientation of which is perpendicular to the 2D sheets. The geometry of the bisSalen in the MOF is not planar. The remaining uncoordinated pyridyl groups point toward the 1D channels. Because of these openly accessible pyridyl groups in the channels, the Zn-bisSalen MOF is a very active catalyst for transesterifications.

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contain dangling metal ions, not in the channels. In such a case, however, the advantages of well-defined channels, for example, substrate selectivity and enhanced efficiency of catalysis, will be marginally effective.

On the other hand, the incorporation of Lewis-basic motifs in the framework is rather challenging because of their reactivity toward metal ions during the preparation of the corresponding MOFs. For example, nonfunctional, symmetric pillar ligands such as 1,4-diazabicyclo[2.2.2]octane (DABCO) or 4,4'-bipyridyl (4,4'-bpy) tend to bridge two metal ions by using two equivalent N-donor atoms to leave no free basic site.^[7] Nevertheless, we recently reported one exceptional case, in which DABCO coordinates with only one N atom to the metal center, and the other N atom is not coordinating.^[8] We may well attribute this unprecedented phenomenon to the geometric constraints of the terphenyl-3,3'-dicarboxylate (3,3'-TPDC) bridging ligand used in that case. The corresponding Zn MOF, Zn(3,3'-TPDC)(DABCO), indeed exhibited catalytic activity for the nitroaldol reaction in a size-dependent manner because of the DABCO, which was orderly located in microporous 1D channels.^[9] Recently, Lewis-basic sites in the channels of MOFs are thought to be beneficial for CO₂ capture applications, because CO2 possesses a higher polarizability and a larger quadrupole moment than N₂, CH₄, and H₂.^[10] As a result, MOFs that have chemically accessible Lewis-basic sites usually exhibit a high CO₂ adsorption enthalpy.

There are numerous reports about postsynthetic framework modifications with IRMOF-3, which consists of metal ions and 2-aminobenzenedicarboxylate (NH₂–BDC) bridging ligands.^[11] The amino functionality remains intact dur-

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ing the MOF synthesis, and thus it can be subsequently utilized for a wide range of chemical reactions to modify the frameworks. Although these MOFs are good catalysts for the Knoevenagel reaction of benzaldehyde because of the free amino groups inside their channels, as reported by Gascon et al.,^[12] the number of publications of MOF-based catalytic systems with functional groups other than NH₂– BDC inside the channels is still limited, because the introduction of catalytically active organic functionalities is much more challenging.

In this contribution, we prepared a new Zn-bisSalen MOF by using the bridging ligand N,N',N'',N'''-tetrakis[3-*tert*-butyl-5-(4-pyridinyl)salicylidene]-1,2,4,5-benzenetetraamine (bisSalen). The Zn-bisSalen MOF contains uncoordinated Lewis-basic pyridyl groups inside its channels. The intact, openly accessible pyridyl group acts as a catalytic center for transesterification reactions with various substrates.

Results and Discussion

A Zn-bisSalen MOF was prepared by the reaction between Zn(NO₃)₂ and the bisSalen ligand N,N',N'',N'''tetrakis[3-tert-butyl-5-(4-pyridinyl)salicylidene]-1,2,4,5benzenetetraamine in N,N-diethylformamide (DEF) at 120 °C. The new bisSalen ligand was prepared according to Scheme 1 by starting from 3-tert-butyl-2-hydroxybenzaldehyde. No additional ligand except the bisSalen was employed during the Zn-bisSalen MOF synthesis. We obtained extremely small, red, block-shaped single crystals $(0.075 \text{ mm} \times 0.068 \text{ mm} \times 0.044 \text{ mm}).$ The Zn-bisSalen MOF crystallized in the monoclinic $P2_1/c$ space group, and its asymmetric unit comprises one half of a centrosymmetric dinuclear complex and half a diethylamine solvate molecule. The crystal was so small that we could not obtain other useful information about the solvate molecules, except one diethylamine group, which could be generated from DEF solvent. The bisSalen ligand bridges two Zn^{II} ions (Figure 1), and one of the pyridyl groups on each side of bisSalen further coordinates to a bisSalen-coordinated Zn^{II} ion of another dinuclear complex to provide a 2D sheet structure, as depicted in Figure 2. The coordinated bisSalen is tilted significantly, and the tilting angles between the middle phenyl group and the side wings, (C5/C6/C7/C8/C9/ C10) and (C22/C23/C24/C25/C26/C27), are 18° and 9°, respectively.

These undulated 2D sheets are stacked closely together to form a 3D-like structure containing 1D channels, as shown in Figure 3. The remaining uncoordinated pyridyl groups point toward these channels (Figure 2). The coordination environment of each Zn^{II} ion is a distorted tetragonal pyramid formed by an equatorial N₂O₂ unit from one side of the bisSalen and an axial pyridyl N atom.

There are very few examples of MOFs containing free pyridyl groups inside channels in the literature,^[13,14] because they tend to coordinate metal ions during the MOF synthesis whenever free metal ions are available. For instance, Kim et al. reported a MOF having a free pyridyl group exposed into a well-defined chiral channel that was formed when they used pyridyl-functionalized D-tartric acid as a bridging ligand.^[13] The pyridyl group exposed toward the channels catalyzed transesterifications in a substrate-size-dependent manner. Chen et al. also prepared a luminescent Eu MOF with well-defined free pyridyl groups orderly located in MOF channels by using pyridine-3,5-dicarboxylate as a bridging ligand.^[14]

On the basis of a PLATON analysis,^[15] the solvent-accessible void volume of the framework was calculated to be 41.1% for the solvent-free Zn-bisSalen MOF. According to analytical data from elemental analysis and thermogravimetric analysis (TGA), there are four diethylamine (DEA) and sixteen water molecules in a unit cell, although we could not precisely locate these solvate molecules because of their disorder in a large void space. Thus, the Zn-bisSalen MOF possesses a very large void space. The as-prepared ZnbisSalen MOF gradually lost weight upon heating up to 445 °C, as shown in Figure 4. Four DEA and sixteen solvate water molecules were completely lost at this temperature. Once the temperature was further increased, the weight gradually decreased further. The bulk purity of the as-prepared sample was confirmed by powder X-ray diffraction (PXRD). As depicted in Figure 5, there is a good agreement between the PXRD pattern of the bulk sample and the pattern simulated from the single-crystal X-ray diffraction data. Thus, the bulk sample was very pure.

The porosity of the Zn–bisSalen MOF was evaluated by a standard volumetric N_2 adsorption–desorption analysis at 77 K. The as-prepared Zn–bisSalen MOF was immersed



Scheme 1. Preparation of the bisSalen ligand with four peripheral pyridyl groups.

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Figure 1. Dinuclear unit of the Zn–bisSalen MOF with atomic labelling. The displacement ellipsoids are shown at the 30% probability level. Unlabelled atoms are related by the symmetry operator (-x, 1 - y, 1 - z).



Figure 2. Structure of the Zn–bisSalen MOF showing uncoordinated pyridyl groups exposed toward 1D channels. Openly accessible pyridyl groups are highlighted as ball-and-stick models. Hydrogen atoms are omitted for clarity.

in chloroform for solvent exchange before it was activated at 120 °C for 1 h. Despite the large solvent-accessible void of the solvent-free Zn–bisSalen MOF, the evacuated Zn– bisSalen MOF only moderately sorbed N₂, which was possibly due to the partial framework collapse after evacuation of the solvent inside the channels. In fact, many known 2D sheet-based frameworks are often flexible, and a change of the original framework structure can be observed.^[16] The Brunauer–Emmett–Teller (BET) surface area was 175 m²/g, and the total pore volume was 0.17 cm³/g. The N₂ adsorption–desorption isotherms depicted in Figure 6 resemble type I isotherms, which is indicative of the microporous



Figure 3. Packing diagram of the 2D sheets of the Zn–bisSalen MOF along the c axis. Each layer is indicated with different colors.



Figure 4. TGA curve for the as-prepared Zn-bisSalen MOF.

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Figure 5. PXRD patterns for the Zn–bisSalen MOF: (a) simulated from single-crystal X-ray diffraction data, (b) obtained from asprepared Zn–bisSalen MOF, and (c) obtained from the Zn–bisSalen MOF after transesterification.

range of the pore structure.^[17] On the basis of the Horvath–Kawazoe (HK) method, the measured pore diameter was 0.92 nm.^[18]

Although the evacuated Zn-bisSalen MOF might partially lose its structure because of the flexible nature of its framework, the as-prepared Zn-bisSalen MOF may act as an efficient heterogeneous Lewis-base catalyst because of the openly accessible pyridyl groups. Also the many solvent and water molecules that occupy the channels of the asprepared Zn–bisSalen MOF can be easily exchanged during catalysis with solution containing substrate molecules, as we previously observed in Zn(3,3'-TPDC)(DABCO) catalysis.^[9] We chose the transesterification reaction as a model reaction for the Zn-bisSalen MOF catalysis, because free pyridyl groups were found to be very active for this reaction.^[13] As depicted in Figure 7, three different acetate substrates were used as substrates for the transesterification reaction in ethanol at 50 °C. The p-nitrophenyl acetate substrate exhibited faster kinetics than phenyl acetate and vinyl acetate. Both phenyl acetate and vinyl acetate showed almost the same rate of reaction.



Figure 7. Timecourse of the transesterifications catalyzed by the aspreapred Zn–bisSalen MOF.

It is noteworthy that *p*-nitrophenyl acetate is larger than the other two substrates. Thus, the faster kinetics for *p*-nitrophenyl acetate may be attributable to electronic effects rather than to the substrate size dependence. This result can be accounted for by the fact that the void of the ZnbisSalen MOF is large enough to accommodate p-nitrophenyl acetate. After the transesterification of *p*-nitrophenyl acetate, we also checked the same reaction, using the hotfiltered solution as a catalyst, to determine whether leached metal ions are the active catalyst or not. In comparison to the original yield of 83%, only a low yield of 10% was observed in this experiment. Therefore, the main catalytic sites are indeed the openly accessible pyridyl groups located in the channels of the Zn-bisSalen MOF. However, in comparison to the as-prepared sample, the retrieved ZnbisSalen MOF catalyst exhibited a PXRD pattern with a very reduced diffraction-peak intensity, as shown in Figure 5. A partial collapse or amorphization of the flexible, 3D-like framework of the Zn-bisSalen MOF induced by a delamination of the 2D sheets may be responsible for this change of the PXRD pattern. Nevertheless, the catalyst maintained its activity for more than 168 h in reagent-grade ethanol, which contains water (ca. 5%). To check the recycl-



Figure 6. (a) N_2 adsorption-desorption isotherms for the Zn-bisSalen MOF at 77 K. (b) Horvath-Kawazoe (HK) pore-size-distribution curve.



ability of the catalyst, we ran the reaction three more times by using the recovered catalyst. Although the conversion of recycling experiment gradually became smaller than the original one (1st recycle 65%; 2nd recycle 55%; 3rd recycle 53%), the Zn–bisSalen MOF indeed exhibited catalytic activity.

Conclusions

We prepared and characterized a new rare example of a Zn–bisSalen MOF containing a metalloligand^[19–21] with catalytically active, openly accessible pyridyl groups pointing toward 1D channels. The planar bisSalen ligand is severely distorted, which results in an interesting 2D sheet structure. Although it is a 2D structure, the 2D sheets stack together to form a 3D-like framework with open porosity. The Zn–bisSalen MOF is an active catalyst for the transesterification of various acetate compounds in ethanol.

Experimental Section

General Methods: All commercially available starting materials and solvents were purchased from Sigma–Aldrich, TCI, and Acros Co. and were used without further purification. All of the reactions and manipulations were carried out under N₂ with standard inert-gas and Schlenk techniques unless otherwise noted. The solvents used in inert-gas reactions were dried by using standard procedures. Flash column chromatography was carried out with 230–400 mesh silica gel purchased from Sigma–Aldrich by using the wet-packing method. All deuterated solvents were purchased from Sigma–Aldrich. 5-Bromo-3-*tert*-butyl-2-hydroxybenzaldehyde and 3-*tert*-butyl-5-(4-pyridinyl)salicylaldehyde were prepared according to modified literature procedures.

Preparation of 5-Bromo-3-*tert***-butyl-2-hydroxybenzaldehyde:** To a solution of 3-*tert*-butyl-2-hydroxybenzaldehyde (1.78 g, 9.98 mmol) in acetic acid (5 mL) was added a solution of bromine (0.53 mL, 10.3 mmol) in acetic acid (2 mL) by using a dropping funnel over the course of 15 min. The resulting mixture was stirred at room temperature for 1 h. The mixture was diluted with CH₂Cl₂ (30 mL) and subsequently washed with H₂O (10 mL), saturated aqueous Na₂CO₃, saturated aqueous NaHCO₃ (10 mL), and brine (10 mL). The organic phase was dried with Na₂SO₄, and the solvents were evaporated to afford pure 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde as a yellow solid (2.28 g, 89% yield). ¹H NMR (CDCl₃): δ = 11.73 (s, 1 H), 9.81 (s, 1 H), 7.58 (d, ³J_{H-H} = 2.4 Hz, 1 H), 7.52 (d, ³J_{H-H} = 2.4 Hz, 1 H), 1.40 (s, 9 H) ppm.

Preparation of 3-*tert***-Butyl-5-(4-pyridinyl)salicylaldehyde:** To a solution of 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (1.0 g, 3.89 mmol) in dioxane (100 mL) were added 4-pyridinylboronic acid (0.7 g, 4.28 mol), a solution of K₂CO₃ (1.34 g, 9.73 mmol) in H₂O (20 mL), PPh₃ (0.1 g, 0.4 mmol), and PdCl₂(PPh₃)₂ (0.28 g, 0.4 mmol). The mixture was degassed with N₂ for 10 min and stirred at 90 °C under N₂ for 3 h. After cooling, the resulting mixture was diluted with CH₂Cl₂ (100 mL) and washed with H₂O and brine two times. The organic layer was separated and dried with anhydrous MgSO₄. After filtration, the filtrate was concentrated to dryness by using a rotary evaporator. The residue was purified by silica-gel column chromatography (CH₂Cl₂/hexanes = 1:4, v/v) to afford pure 3-*tert*-butyl-5-(4-pyridinyl)salicylaldehyde as a yellow solid (0.850 g, 59% yield). ¹H NMR (CDCl₃): δ = 11.93 (s, 1 H),

9.98 (s, 1 H), 8.67 (d, ${}^{3}J_{H-H} = 6.1$ Hz, 2 H), 7.81 (d, ${}^{3}J_{H-H} = 2.5$ Hz, 2 H), 7.69 (d, ${}^{3}J_{H-H} = 2.5$ Hz, 1 H), 7.48 (d, ${}^{3}J_{H-H} = 6.1$ Hz, 1 H), 1.48 (s, 9 H) ppm.

Preparation of N, N', N'', N'''-Tetrakis[3-tert-butyl-5-(4-pyridinyl)salicylidene]-1,2,4,5-benzenetetraamine: To a solution of 1,2,4,5benzenetetramine tetrahydrochloride (0.223 g, 0.78 mmol) in pyridine (10 mL) and ethanol (10 mL) was added dropwise a solution of 3-tert-butyl-5-(4-pyridinyl)salicylaldehyde (1.0 g, 3.9 mmol) in ethanol (20 mL) at room temperature. The mixture was heated to reflux for 15 h. After cooling, the mixture was filtered, and the solid was washed with ethanol three times and dried to afford N,N',N'',N'''-tetrakis[3-tert-butyl-5-(4-pyridinyl)salicylidene]-1,2,4,5-benzenetetraamine (bisSalen) as a red solid (0.630 g, 59% yield). ¹H NMR ([D₆]DMSO): δ = 12.05 (br., 4 H), 10.13 (s, 4 H), 8.75 (d, ${}^{3}J_{H-H} = 6.3$ Hz, 8 H), 8.69 (s, 2 H), 8.29 (d, ${}^{3}J_{H-H} = 2.3$ Hz, 4 H), 7.96 (d, ${}^{3}J_{H-H} = 2.3$ Hz, 4 H), 7.95 (d, ${}^{3}J_{H-H} = 6.3$ Hz, 8 H) 1.48 (s, 36 H) ppm. ¹³C NMR ([D₆]DMSO): δ = 199.27, 161.72, 148.87, 139.05, 132.83, 132.10, 128.18, 127.85, 122.02, 121.78, 54.09, 35.44, 29.63 ppm. MS (MALDI-TOF): calcd. for [M]⁺ 1087.356; found 1086.48.

Preparation of the Zn-bisSalen MOF: $Zn(NO_3)_2$ ·6H₂O (0.015 g, 0.05 mmol) and the bisSalen ligand (0.027 g, 0.025 mmol) were dissolved in *N*,*N*-diethylformamide (10 mL). The reaction mixture was heated at 120 °C in a Teflon-lined reactor for 3 d. Red microcrystals were retrieved by filtration, washed with *N*,*N*-diethylformamide, and dried in air. $C_{86}H_{142}N_{12}O_{20}Zn_2$ (1794.9): calcd. C 57.55, H 7.97, N 9.36; found C 57.29, H 5.73, N 9.79.

Transesterification: A mixture of the as-prepared Zn–bisSalen MOF catalyst (0.005 g, 0.0046 mmol), an ester of choice [0.276 mmol (*p*-nitrophenyl acetate, 0.050 g; phenyl acetate, 0.038 g; vinyl acetate, 0.024 g)], and *n*-nonane (10 μ L, 0.056 mmol) as an internal standard in ethanol (10 mL) was heated at 50 °C with constant stirring for 168 h. The reaction progress was monitored at a regular interval by taking an aliquot and analyzing it by gas chromatography. A recycling experiment was performed by using catalyst that was recovered from a previous reaction by centrifugation (9000 rpm, 20 min).

Physical Measurements: NMR spectra were recorded with a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts were referenced to the proton resonance resulting from the protic residue in the deuterated solvent, and ¹³C chemical shifts were recorded downfield in ppm relative to the carbon resonance of the deuterated solvent. Matrix-assisted laser-desorption-ionization time-of-flight mass spectra (MALDI-TOF) were obtained with a Bruker Daltonics LRF20 MALDI-TOF mass spectrometer at the Industry-Academic Cooperation Foundation, Yonsei University. The N2 adsorption-desorption analysis was performed with a Belsorp-miniII at 77 K (BEL Japan). The CHCl₃ exchanged sample was dried at 120 °C for 1 h prior to the measurement. Powder X-ray diffraction patterns were obtained by using a Rigaku MiniFlex (30 kV, 15 mA). Thermogravimetric analyses were carried out with a TGA Q5000 (TA Instruments) under nitrogen. Elemental analyses were performed at the Organic Chemistry Research Center (Seoul, Korea) by using an EA1112 (CE Instruments, Italy).

X-ray Crystallography: A clear, red, block-shaped single crystal of Zn–bisSalen MOF ($C_{74}H_{66}N_9O_4Zn_2$) with the approximate dimensions of 0.075 mm \times 0.068 mm \times 0.044 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured with a Bruker AXS X8 Prospector system equipped with a multilayer monochromator and a Cu IµSTM microfocus sealed-tube X-ray source ($\lambda = 1.54178$ Å). A total of 2031 frames were col-

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Table	1.	Selected	bond	lengths	[A]	and	angles	[°]	
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Zn(1)–O(1)	1.935(11)	Zn(1)–O(2)	1.956(12)
Zn(1)–N(3)#1	2.084(14)	Zn(1)-N(2)	2.098(14)
Zn(1)-N(1)	2.100(13)		
		_	_
O(1)–Zn(1)–O(2)	94.8(5)	O(1)–Zn(1)–N(3) #1	101.7(5)
O(2)–Zn(1)–N(3)#1	106.2(5)	O(1)-Zn(1)-N(2)	159.3(5)
O(2) - Zn(1) - N(2)	88.2(5)	N(3)#1-Zn(1)- N(2)	97.1(5)
O(1)-Zn(1)-N(1)	89.9(5)	O(2) - Zn(1) - N(1)	149.5(5)
N(3)#1- $Zn(1)$ - $N(1)$	102.3(5)	N(2) - Zn(1) - N(1)	77.5(5)

lected. The total exposure time was 27.46 h. The frames were integrated with the Bruker SAINT software package by using a wideframe algorithm. The integration of the data with a monoclinic unit cell yielded a total of 11994 reflections to a maximum θ angle of 44.50° (1.10 Å resolution), of which 3123 were independent (average redundancy 3.976, completeness = 90.7%, $R_{\text{int}} = 7.54\%$, $R_{\rm sig} = 15.17\%$) and 1441 (46.14%) were larger than $2\sigma(F^2)$. The final cell constants of a = 10.4189(12) Å, b = 18.863(2) Å, c =22.224(3) Å, $\beta = 91.451(9)^\circ$, V = 4366.3(9) Å³, are based upon the refinement of the XYZ centroids of 3258 reflections above $20\sigma(I)$ with $6.146^{\circ} < 2\theta < 85.72^{\circ}$. The data were corrected for absorption effects by using the multiscan method (SADABS). The ratio of minimum/maximum apparent transmission was 0.825. The structure was solved and refined by using the Bruker SHELXTL Software Package in the space group $P2_1/c$ with Z = 2 for the formula unit $C_{74}H_{66}N_9O_4Zn_2$. The final anisotropic full-matrix leastsquares refinement on F^2 with 393 variables converged at R_1 = 12.47% for the observed data and at $wR_2 = 29.49\%$ for all data. The goodness-of-fit was 1.096. The largest peak in the final difference-electron-density synthesis was 0.653 e⁻/Å³, and the largest hole was $-0.484 \text{ e}^{-/\text{Å}^3}$ with an RMS deviation of $0.127 \text{ e}^{-/\text{Å}^3}$. On the basis of the final model, the calculated density was 0.971 g/cm³ and F(000), 1330 e⁻. Selected bond lengths and angles are listed in Table 1. CCDC-896260 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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