Synthesis and Structure of a Helical Coordination Polymer: $\{[Zn_2(bdaip)(\mu\text{-}OH)(OH)]NO_3\cdot 2H_2O\}_\infty$ (Hbdaip = 2,6-Bis{*N*-[2-(dimethylamino)ethyl]-iminomethyl}-4-methylphenol)

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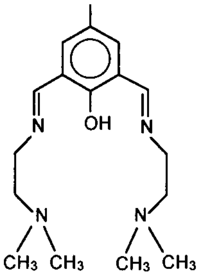
Introduction

Phenol-based compartmental ligands are often used to stabilize dinuclear metal cores.[1−7] The Schiff base ligand 2,6-bis{*N*-[2-(dimethylamino)ethyl]iminomethyl}-4-methylphenol (Hbdaip) bridges two zinc ions through the deprotonated phenolic oxygen, thus providing three donor atoms for each metal center. In the dinuclear complexes $[Zn_2(bdaip)(\mu\text{-}Cl)Cl_2]$ and $[Zn_2(bdaip)(\mu\text{-}CH_3CO_2)_2]ClO_4$ the remaining coordination sites are saturated by coordinating anions.[8] Here we report on the aggregation of $[Zn_2(bdaip)(\mu\text{-}OH)]^{2+}$ units to a 1D coordination polymer containing single hydroxo bridges, when the weakly coordinating nitrate is present as a counterion. The formation of hydroxo-bridged discrete di- and oligonuclear complexes is a common feature in Zn coordination chemistry; however, interestingly X-ray analysis of the title compound revealed an infinite, 6_1-helical $\{Zn_2(\mu\text{-}OH)\}_\infty$ chain which represents to our knowledge an unprecedented structural motif in hydroxo-bridged Zn complexes.



Hbdaip

Experimental Section

Table 1. Crystallographic Data

empirical formula	$C_{17}H_{33}N_5O_8Zn_2$
fw	566.22
space group	$P6_1$
a, Å	11.340(1)
c, Å	32.984(1)
V, Å^3	3673.3(5)
Z	6
d(calcd), g cm^{-3}	1.536
μ(Mo Kα), mm^{-1}	2.008
T, K	293
R1, wR2 [$I > 2\sigma(I)$]^a	0.054, 0.140
R1, wR2 (all data)^a	0.078, 0.163

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0984P)^2$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Zn(1)−N(1)	2.082(8)	Zn(2)−N(3)	2.088(7)
Zn(1)−N(2)	2.213(7)	Zn(2)−N(4)	2.171(7)
Zn(1)−O(1)	2.102(6)	Zn(2)−O(1)	2.066(5)
Zn(1)−O(2)	2.003(6)	Zn(2)−O(2)	2.015(5)
Zn(1)−O(3)	1.949(6)	Zn(2)−O(3a)	1.960(6)
Zn(1)···Zn(2)	3.161(1)	Zn(1a)···Zn(2)	3.673(1)
N(1)−Zn(1)−O(1)	80.7(3)	N(3)−Zn(2)−O(1)	81.6(2)
N(1)−Zn(1)−O(2)	134.6(3)	N(3)−Zn(2)−O(2)	142.0(2)
N(1)−Zn(1)−O(3)	114.5(3)	N(3)−Zn(2)−O(3a)	108.2(3)
N(1)−Zn(1)−N(2)	81.6(3)	N(3)−Zn(2)−N(4)	80.0(3)
O(1)−Zn(1)−O(2)	78.3(2)	O(1)−Zn(2)−N(4)	149.7(3)
O(1)−Zn(1)−N(2)	154.3(3)	Zn(1)−O(1)−Zn(2)	98.7(2)
Zn(1)−O(2)−Zn(2)	103.8(3)	Zn(1a)−O(3a)−Zn(2)	140.0(4)

General. 2,6-Diformyl-4-methylphenol was prepared according to ref 9. All chemicals and solvents were reagent grade and used without further purification. The ^{1}H NMR spectrum was recorded on a Bruker AC200 spectrometer using sodium 3-(trimethylsilyl)propanesulfonate as internal reference. The infrared spectrum was taken on a Bruker IFS 28 FT spectrometer.

$\mathbf{\{[Zn_2(bdaip)(\mu\text{-}OH)(OH)]NO_3\cdot 2H_2O\}_\infty}$ **1.** 2,6-Diformyl-4-methylphenol (100 mg, 0.61 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (362 mg, 1.22 mmol), and *N*,*N*-dimethylethylenediamine (107 mg, 1.21 mmol) were dissolved in ethanol−water (2:1, 30 mL) and stirred at room temperature overnight. The deep yellow solution was brought to pH 10.2 by 2 N NaOH and kept at the ambient temperature in an open beaker. After a few days, X-ray suitable crystals of $\{[Zn_2(bdaip)(\mu\text{-}OH)(OH)]NO_3\cdot 2H_2O\}_\infty$ were obtained. Yield: 183 mg (53%). Selected IR data (cm^{-1}): 3151 (br), 2839 (m), 2799 (m), 1644 (s), 1622 (s), 1517 (s), 1456 (m), 1384 (s), 1284 (w), 1238 (m), 1077 (m), 1023 (m), 893 (m), 826 (m), 780 (m), 388 (m). ^{1}H NMR (DMSO-d_6): δ = 8.12 (s, 2H, azomethine), 6.85 (s, 2H, aryl), 3.58 (s, br, 4H, =*N*−CH$_2$), 2.81 (s, br, 4H, −*N*−CH$_2$), 2.42 (s, 12H, *N*−CH$_3$), 2.20 (s, 3H, *Ar*−CH$_3$).

Anal. Calcd for $C_{17}H_{33}N_5O_8Zn_2$ (M_r = 566.2): C, 36.1; H, 5.9; N, 12.4. Found: C, 36.1; H, 5.6; N, 12.4.

Crystal Structure Analysis. Crystal data were collected at room temperature on an Enraf-Nonius-KappaCCD diffractometer[10] using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were applied.[11] The structure was solved by conventional Patterson methods and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 using the SHELXTL PLUS and SHELXL-93 programs.[12] The scattering factors were those given in the SHELXTL PLUS program. The refinement was carried out in the enantiomorphous space groups $P6_1$ and $P6_5$. The Flack's parameter[13] converged to x = 0.50(3) ($P6_1$) and 0.52(3) ($P6_5$) indicating racemic twinning, which was

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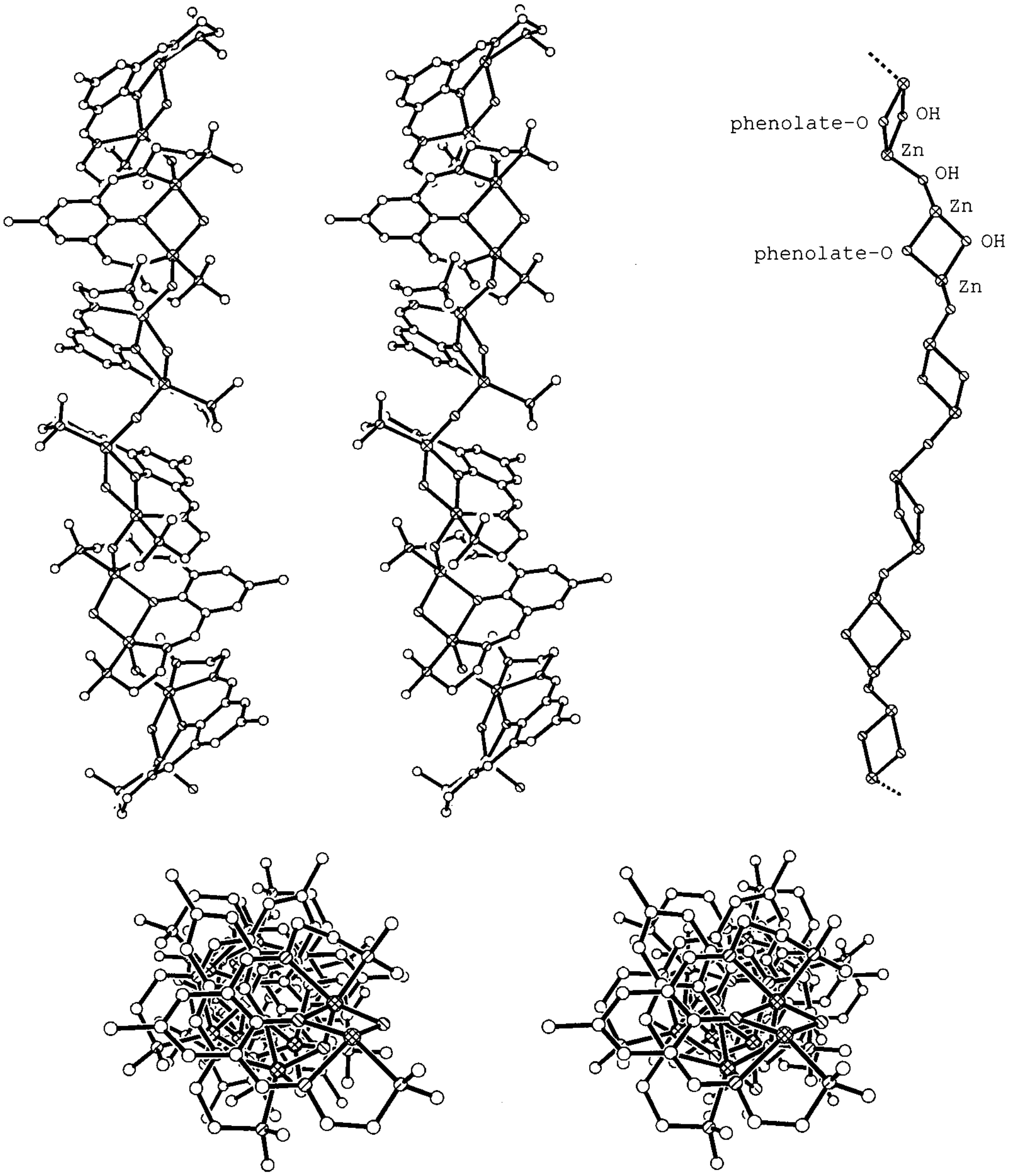

Figure 1. Section of the 6_1-helical coordination polymer of **1**. Top: side view (stereoview) and view of the helical backbone. Bottom: stereoview down the helix axis. Zn: crosshatched circles. N,O: hatched circles. C: empty circles.

taken into account during the final cycles of least squares refinement. All non-hydrogen atoms were refined anisotropically (with the exception of C(10), C(11), water molecules of crystallization, and the nitrate nitrogen and oxygens). Carbon-bound hydrogen atoms were placed at calculated positions and given fixed isotropic temperature factors.

Crystallographic data and details of refinement are reported in Table 1. Selected bond lengths and angles are listed in Table 2.

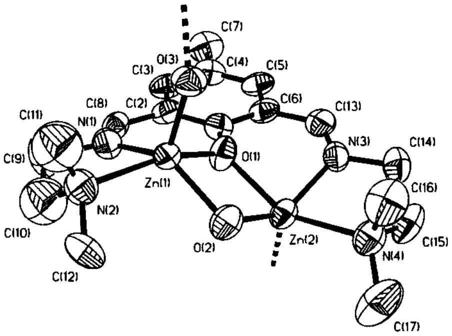

Figure 2. Asymmetric unit of the crystal structure of **1** with the atom-numbering scheme. Nitrate and water of crystallization are omitted for clarity.

Results and Discussion

Condensation of 2,6-diformyl-4-methylphenol with 2 equiv of *N*,*N*-dimethylethylenediamine in the presence of $Zn(NO_3)_2 \cdot 6H_2O$ in aqueous solution followed by addition of base gave yellow needles of $\{[Zn_2(bdaip)(\mu\text{-}OH)(OH)]NO_3 \cdot 2H_2O\}_\infty$ (**1**). Views of the helical motif in **1** are displayed in Figure 1; selected bond lengths and angles are listed in Table 2. The structure is built up of dinuclear $\{Zn_2(bdaip)(\mu\text{-}OH)\}^{2+}$ entities (Figure 2) that are connected through single hydroxo bridges. Within the subunits, the five-coordinate Zn ions are bridged by the deprotonated phenolic oxygen of the ligand and a hydroxo group at a distance of 3.161(1) Å. Further donor atoms are the imine and amine nitrogens of the ligand side arms. The Zn−O−Zn bond angles fall in the typical range found for bis(μ-oxo)dizinc cores; the Zn···Zn separation is slightly longer than the values reported for comparable compounds.[14] The coordination geometry of Zn is best described as distorted square-pyramidal; the structural indices τ^{15} indicating the relative amount of trigonality (square pyramid $\tau = 0$, trigonal bipyramid $\tau = 1$) are 0.33

[Zn(1)] and 0.13 [Zn(2)]. The Zn ions are displaced by 0.476(3) Å [Zn(1)] and 0.464(3) Å [Zn(2)] out of the least-squares planes defined by the respective equatorial donor atoms N(1), N(2), N(3), N(4), O(1), and O(2). The axial positions are occupied by the hydroxo group that links the subunits to each other resulting in an infinite $Zn_2(\mu\text{-OH})$ strand following a 6_1 (or 6_5, see below) screw axis. The mono-μ-hydroxo-bridged Zn ions are 3.673(1) Å apart, which is at the high end of the range found for oligonuclear Zn complexes with single hydroxo bridges.[14,16] The Zn−O−Zn angle of 140.0(4)° compares well with the values reported for mono(μ-hydroxo)dizinc complexes. The pitch height of the helix is equal to the length of the crystallographic *c* axis [32.984(1) Å]. Twelve Zn ions span one helical turn so that the helix is considerably stretched. Adjacent ligands form a dihedral angle of 39.2(2)°. Since the ligand itself is achiral, equal amounts of *P*- and *M*-helices are formed. The two enantiomers crystallize in the enantiomorphous space groups $P6_1$ and $P6_5$, and, as often observed in chiral space groups,[17] twinned crystals containing domains of opposite helicity were obtained. Thus, **1** is another example for homochiral packing of helices derived from achiral building blocks,[18] although only partial self-resolution of the racemate occurs. The diameter of the helix is approximately 8 Å. The distance between the axes of neighboring helices extending along the *c* axes of the unit cells in the crystal lattice is 11.340 Å. The channels with diameters of about 3 Å between the helices are filled with nitrate anions and water molecules of crystallization that are connected through hydrogen-bonding interactions [O(1w)···O(2w) 2.71(2) Å; O(1w)···O(5) 2.79(2) Å, x, $y + 1$, z; O(4)···O(2w) 2.85(3) Å, $x - y$, x, $z + {}^1/_6$]. Short contacts are also observed between the bridging hydroxo groups and nitrate oxygens [O(2)···O(6) 2.97(2) Å, $x + 1$, $y + 1$, z] as well as water of crystallization [O(2)···O(2w) 2.87(2) Å, $x + 1$, y, z].

The polymeric nature of **1** is likely a consequence of the weak coordinating abilities of the nitrate anion. The ligand providing three donor atoms for each metal center leaves vacant coordination sites at the Zn ions that can be saturated by anions as found in $[Zn_2(bdaip)(\mu\text{-Cl})Cl_2]$ and $[Zn_2(bdaip)(\mu\text{-}CH_3CO_2)_2]ClO_4$[8] or by aggregation of the dinuclear entities to species with higher nuclearity. Discrete oligonuclear Zn complexes have been obtained with related binucleating ligands,[19] e.g., $[Mg(H_2O)_6][\{Zn_2L(CH_3CO_2)\}_2(\mu_3\text{-OH})_2]\cdot 6H_2O$ (H_3L = Schiff base prepared from 2,6-diformyl-4-methylphenol and glycine) containing a $Zn_4(\mu_2\text{-OAr})_2(\mu_3\text{-OH})_2$ core.[19a] The formation of an infinite chain in **1** rather than a similar tetranuclear complex may be attributed to steric hindrance due to the *N*-methyl groups.

Helicity is a topic of increasing interest in coordination chemistry and materials science, and metal complexes exhibiting helical conformations receive much current attention.[20−33] In recent years, much effort has been devoted to the preparation of helical metal complexes (helicates) by careful design of helicating ligands, in particular oligopyridines.[20,21] However, there are also examples, where—like in **1**—helicity spontaneously arises. The majority of helical compounds reported to date are discrete oligonuclear compounds, while infinite 1D coordination polymers assuming a helical conformation are less often found.[22−33]

Furthermore it is notable that single hydroxo bridges occur in **1**. While a large number of multiply bridged Zn complexes have been reported, examples of compounds containing single, unsupported hydroxo bridges are less numerous.[14,16]

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Supporting Information Available: Packing diagram of compound **1**. Crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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