

The Crystal Structure of One-Dimensional Carboxylate-Bridged Zinc(II) Complex with Bis(2-Pyridylmethyl)Amino-4-Butyric Acid

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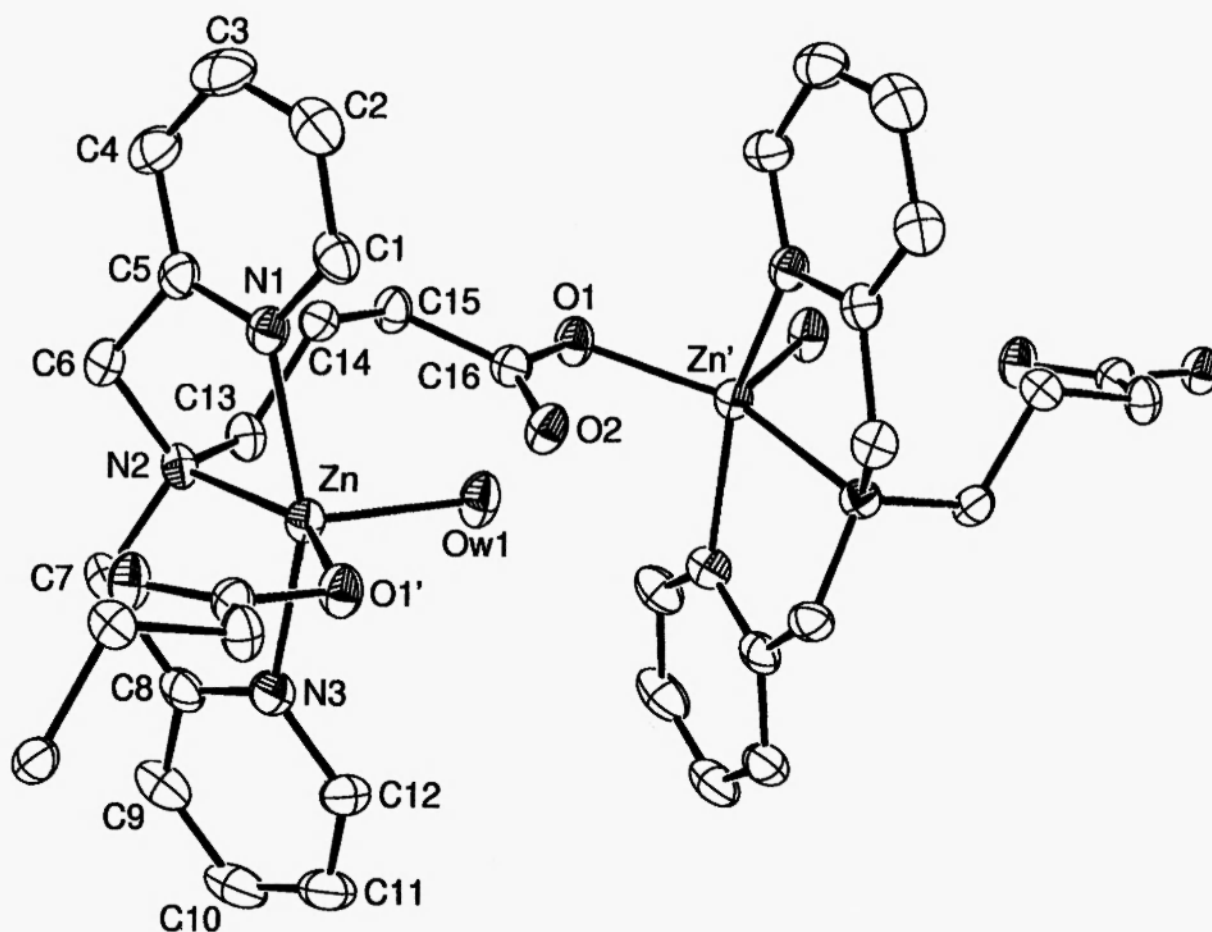


Figure 1. An ORTEP drawing of $\{[\text{Zn}(\mu\text{-pmba})(\text{H}_2\text{O})](\text{ClO}_4)\cdot 4\text{H}_2\text{O}\}_n$ with the atomic labelling scheme (30% probability ellipsoids shown). The perchlorate anions, lattice water molecules, and hydrogen atoms are omitted for clarity. Selected bond distances and angles: Zn-N(1) 2.112(6), Zn-N(2) 2.160(5), Zn-N(3) 2.108(6), Zn-O(1)#1 1.997(5), Zn-Ow(1) 2.022(5), Zn $\cdots$ Zn 6.877(2) Å; N(1)-Zn-N(2) 78.9(2), N(1)-Zn-N(3) 156.1(2), N(2)-Zn-N(3) 78.6(2), O(1)#1-Zn-N(1) 98.1(2), O(1)#1-Zn-N(2) 151.0(2), O(1)#1-Zn-N(3) 97.7(2), N(1)-Zn-Ow(1) 99.1(2), N(2)-Zn-Ow(1) 109.7(2), N(3)-Zn-Ow(1) 96.0(2), O(1)#1-Zn-Ow(1) 99.3(2)°. Symmetry transformation: #1 = $x-1/2, -y+1/2, z-1/2$.

COMMENT

The reaction of the pmba ligand containing the carboxylate group with zinc(II) perchlorate leads to a syn-anti carboxylate-bridged complex. The zinc atoms are bridged by syn-anti carboxylate group of the pmba ligand to form a polymeric one-dimensional chain with Zn...Zn separation of 6.877(2) Å (Fig. 1). Each zinc atom reveals a distorted square-pyramidal coordination, in which the basal plane is made up by the three nitrogen atoms of the ligand and one oxygen atom belonging to the carboxylate group of an adjacent molecule, while a water molecule is coordinated at the axial position. The geometry is somewhat distorted from square-pyramidal, as is apparent from the observed τ value of 0.09 [1]. The zinc atom is displaced 0.304(2) Å from the least-squares plane defined by the N₃O basal plane toward the water molecule. The dihedral angle between the plane of the carboxylate group and ZnN₃O plane is 83.5(3)°. The Zn-Ow(1) linkage is bent slightly off the perpendicular to the ZnN₃O plane by 6.0–19.7°. The secondary Zn-N(1) and Zn-N(3) bond distances are much shorter than the tertiary Zn-N(2) distance, indicating comparatively strong coordination.

EXPERIMENTAL

Synthesis of bis(2-pyridylmethyl)amino-4-butyric acid (pmba)

To water solution (25 mL) of 2-picolyl chloride hydrochloride (3.61 g, 22 mmol) was added a water solution (25 mL) of 4-aminobutyric acid (1.03 g, 10 mmol) and sodium hydroxide (1.6 g, 40 mmol). After the mixture was heated to reflux for one day, the solution was extracted with chloroform. The removal of the solvent yielded the crude white product, which was purified by recrystallization from a 1:1 water-ethanol mixture (10 mL, v/v). Yield: 2.05 g (72%). Anal. Calc. for C₁₆H₁₉N₃O₂: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.43; H, 6.62; N, 14.65%.

Synthesis of {[Zn(μ-pmba)(H₂O)](ClO₄)·4H₂O}_n

A water solution (20 mL) of Zn(ClO₄)₂·6H₂O (186 mg, 0.5 mmol) and pmba (143 mg, 0.5 mmol) was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered and allowed to stand for a few days until colorless crystals formed. The product was filtered and recrystallized from 10 mL of water/ethanol mixture (1/1, v/v). Yield: 155 mg (72%). Anal. Calc. for C₁₆H₂₈ClN₃O₁₁Zn: C, 35.64; H, 5.23; N, 7.79. Found: C, 35.72; H, 5.11; N, 7.65%. IR (KBr, cm⁻¹): ν(CO) 1609, 1420; pyridine skeleton 1557, 1482, 1449; ν(Cl-O) 1093.

Crystallography

An empirical absorption correction was applied [2]. All atoms except for Ow(2), Ow(3) and Ow(4), including hydrogen atoms, were refined anisotropically. All hydrogen atoms were placed in calculated positions allowing to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}. The two hydrogen atoms of Ow(1)

were found from a difference Fourier map and their positions were fixed with U_{iso} to be 1.2 times. The rest of the water molecules were not found.

Table 1
Crystallographic data for $\{[Zn(\mu\text{-pmba})(H_2O)](ClO_4)\cdot 4H_2O\}_n$

Formula	$C_{16}H_{28}ClN_3O_{11}Z$	Formula weight	539.23
Crystal system	n	Crystal size, mm	$0.3 \times 0.2 \times 0.2$
Space group	Monoclinic	a , Å	9.136(5)
b , Å	$P2_1/n$	c , Å	12.816(5)
β , °	19.884(5)	V , Å ³	2253.1(16)
Z	104.59(1)	Diffractionmeter	Enraf-Nonius CAD4
Temperature, K	4	$\mu(\text{Mo-K}\alpha)$, cm ⁻¹	1.270
$F(000)$	293(2)	D_{calcd} , g cm ⁻³	1.590
Reflns meas.	1120	θ_{max} , °	24.95
Reflns with $I > 2\sigma(I)$	4138	Reflns unique, R_{int}	3954, 0.0361
R , wR (F^2 , obs. Data)	2721	R , wR (F^2 , all data)	0.1163, 0.2333
GoF	0.0727, 0.2053	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1394P)^2 + 3.6552P]$
Program used	1.060		where $P = (F_o^2 + 2F_c^2)/3$
	SHELXS-97 /3/, SHELXL-97 /4/, ORTEP /5/	ρ , e Å ⁻³	1.106, -0.705
		Deposition number	CCDC 215292

ACKNOWLEDGEMENTS

This work was supported by grant (No. R05-2003-000-10536-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

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