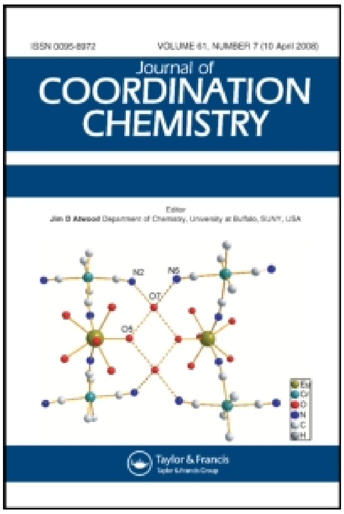

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A novel dimeric zinc(II) complex with a tripodal peptide ligand: a structure stabilized by ligand sharing

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A NOVEL DIMERIC ZINC(II) COMPLEX WITH A TRIPODAL PEPTIDE LIGAND: A STRUCTURE STABILIZED BY LIGAND SHARING

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The crystal structure of a novel dimeric zinc(II) complex, $[ZnL(H_2O)]_2(ClO_4)_2 \cdot 4H_2O$ (L = *N*-(bis(2-pyridyl)-methyl)-2-pyridinecarboxamide), has been determined by X-ray diffraction. In this complex each planar N_{py}–N_{amido}–N_{py} moiety of the ligand coordinates to one zinc ion and the pendant pyridine of one [ZnL] unit completes the coordination sphere of a [ZnL] neighbor. Units of the complex are connected in a two-dimensional network by intermolecular hydrogen bonds. The thermodynamic properties of the ligand with bivalent metal ions Co(II), Ni(II), Cu(II) and Zn(II) were studied by potentiometric titration and the order of the stability constants is in agreement with the Irving–Williams series. The dimeric complex is stabilized through ligand sharing, as confirmed by the crystal structure and thermodynamic properties.

Keywords: Zinc(II) complex; Tripodal peptide ligand; Ligand sharing; Thermodynamic properties

INTRODUCTION

Modeling strategies for the active sites of hemocyanin and tyrosinase have made use of a variety of ligand systems, most of which possess N-heterocycles as potential coordinating groups [1,2]. Designed ligands with pendant donor groups have been used to synthesize ligand-shared dimeric copper(II) complexes [3,4]. Ligands with enough flexibility can give rise to situations where both monomers and the corresponding ligand-shared dimers exist in equilibrium in reaction mixtures [5,6].

The amidate function participates in the coordination chemistry of iron-containing biomolecules such as the anti-tumor drug bleomycin and nitrile hydratase [7,8]. The strong donor ability of a deprotonated amide is expected to imbue the metal center to which it is coordinated with novel electronic properties. Several designed ligands with pyridine-2-carboxamide units were synthesized recently by different groups and their coordination properties with transition metal ions explored [9,10]. However, reports on dimeric zinc(II) complexes are scarce. To extend the range of the pyridine-2-carboxamide ligands, we have synthesized the ligand

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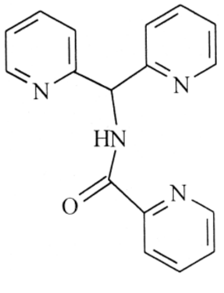
N-(bis(2-pyridyl)methyl)-2-pyridinecarboxamide (L, Scheme 1) [11]. In this paper, we report the synthesis, crystal structure and thermodynamic properties of a novel dimeric zinc(II) complex that is stabilized by ligand sharing.



SCHEME 1

EXPERIMENTAL

General

Infrared spectra were recorded on a Euinox 55 FT spectrophotometer (Bruker), using KBr disks. Elemental analyses were performed on a Perkin Elmer 240C instrument. Stability constants of the complexes were measured on a Beckman Φ71 pH instrument equipped with a 39841 combined electrode. The ligand (L) was prepared as described previously [11].

Preparation of $[ZnL(H_2O)]_2(ClO_4)_2{\cdot}4H_2O$

$Zn(ClO_4)_2{\cdot}6H_2O$ (37.2 mg, 0.1 mmol) in methanol (10 cm^3) was added to L (29.0 mg, 0.1 mmol) in methanol (10 cm^3) and the pH of the solution was adjusted to 8–9 with triethylamine. The solution was stirred for 1 h and the filtrate allowed to stand at room temperature for 2 weeks. Colorless crystals of the complex suitable for X-ray analysis were obtained by slow evaporation. Anal. Calcd. for $C_{34}H_{38}Cl_2N_8O_{16}Zn_2$(%): C, 40.14; H, 3.74; N, 11.02. Found: C, 40.48; H, 3.55; N, 11.36. IR (KBr pellet, cm^{-1}) 3396 (br, vs), 3068 (m), 1610 (s, ν_{CO}), 1591 (s), 1563 (s), 1474 (m), 1436 (m), 1391 (s), 1282 (m), 1087 (vs, ν_{ClO_4}), 764 (s), 703 (m), 626 (m), 599 (m).

Potentiometric Titrations

Potentiometric titrations were carried out at 298.0 ± 0.1 K according to a reported method [12]. The concentrations of the ligand and the metal ions were 1×10^{-3} mol dm^{-3} and the ionic strength was adjusted to 0.1 mol dm^{-3} with KNO_3. Calculations were carried out with the curve-fitting program TITFIT [12].

Crystal Structure Determination

A colorless single crystal of the title complex having approximate dimensions $0.24 \times 0.20 \times 0.16$ mm was mounted on a Bruker Smart 1000 diffractometer equipped

TABLE I Crystal data and structure refinement details for $[ZnL(H_2O)]_2(ClO_4)_2{\cdot}4H_2O$

Empirical formula	$C_{34}H_{38}Cl_2N_8O_{16}Zn_2$
Formula weight	1016.36
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 11.021(4)$ Å, $\alpha = 78.029(6)°$ $b = 14.138(5)$ Å, $\beta = 74.275(6)°$ $c = 14.333(5)$ Å, $\gamma = 88.789(6)°$
Volume	2101.5(12) $Å^3$
Z, Calculated density	2, 1.606 $Mg\,m^{-3}$
Absorption coefficient	1.348 mm^{-1}
$F(000)$	1040
Crystal size	0.24 × 0.20 × 0.16 mm
θ range for data collection	1.51–26.42°
Limiting indices	$-11 \le h \le 13$, $-13 \le k \le 17$, $-17 \le l \le 16$
Reflections collected/unique	12165/8527 [R(int) = 0.0370]
Completeness to $\theta = 26.42$	98.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.820
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8527/19/587
Goodness-of-fit on F^2	0.984
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0522$, $wR2 = 0.1136$
R indices (all data)	$R1 = 0.1085$, $wR2 = 0.1405$
Largest diff. peak and hole	0.438 and −0.584 e $Å^{-3}$

with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature to $2\theta_{max} = 26.42°$ with index ranges $-11 \le h \le 13$, $-13 \le k \le 17$, $-17 \le l \le 16$, with a total of 12 165 reflections being collected, including 8527 independent reflections ($R_{int} = 0.0370$). A summary of the crystallographic data is given in Table I. The structure was solved by direct methods using SHELXS-97 [13]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [14]. Selected bond distances and angles are listed in Table II.

RESULTS AND DISCUSSION

Crystal Structure

The structure of the dimeric cation of the title complex is shown in Fig. 1. The cation is asymmetric and consists of two unsaturated [ZnL] units in which each zinc(II) center has distorted square pyramidal geometry. The pendant pyridine arm of one [ZnL] unit completes the coordination sphere of the other [ZnL] neighbor (*trans* to the carboxamido nitrogen). The mode of ligand sharing of L is similar to that in the complex $[CuLCl]_2{\cdot}8H_2O$ [6]. In the cation, the N_{py}–N_{amido}–N_{py} moiety of the ligand is planar and maintains angles of 155.53(14)° [N(3)–Zn(1)–N(1)] and 156.69(15)° [N(5)–Zn(2)–N(7)] at the zinc(II) centers. Two water molecules occupy the outer axial sites of the two zinc centers and the inner axial positions are vacant. The zinc(II)–N_{amido}

TABLE II Selected bond lengths (Å) and angles (°) for $[ZnL(H_2O)]_2(ClO_4)_2{\cdot}4H_2O$

Zn(1)–N(2)	2.012(3)	Zn(1)–O(3)	2.050(3)
Zn(1)–N(8)	2.051(4)	Zn(1)–N(3)	2.158(4)
Zn(1)–N(1)	2.188(4)	Zn(2)–N(6)	1.996(4)
Zn(2)–N(4)	2.069(4)	Zn(2)–O(4)	2.073(3)
Zn(2)–N(5)	2.158(4)	Zn(2)–N(7)	2.171(4)
N(2)–C(6)	1.323(5)	N(6)–C(23)	1.324(6)
O(1)–C(6)	1.246(5)	O(2)–C(23)	1.238(5)
N(2)–Zn(1)–O(3)	107.37(13)	N(2)–Zn(1)–N(8)	153.26(14)
O(3)–Zn(1)–N(8)	99.34(14)	N(2)–Zn(1)–N(3)	78.44(14)
O(3)–Zn(1)–N(3)	90.39(13)	N(8)–Zn(1)–N(3)	102.96(14)
N(2)–Zn(1)–N(1)	78.29(14)	O(3)–Zn(1)–N(1)	89.37(13)
N(8)–Zn(1)–N(1)	101.22(14)	N(3)–Zn(1)–N(1)	155.53(14)
N(6)–Zn(2)–N(4)	153.19(15)	N(6)–Zn(2)–O(4)	107.81(14)
N(4)–Zn(2)–O(4)	98.41(14)	N(6)–Zn(2)–N(5)	79.54(14)
N(4)–Zn(2)–N(5)	104.51(14)	O(4)–Zn(2)–N(5)	94.04(14)
N(6)–Zn(2)–N(7)	77.60(15)	N(4)–Zn(2)–N(7)	97.96(15)
O(4)–Zn(2)–N(7)	88.66(14)	N(5)–Zn(2)–N(7)	156.69(15)
O(1)–C(6)–N(2)	126.3(4)	O(1)–C(6)–C(5)	119.5(4)
N(2)–C(6)–C(5)	114.2(4)	O(2)–C(23)–N(6)	126.2(4)
O(2)–C(23)–C(22)	119.5(4)	N(6)–C(23)–C(22)	114.3(4)

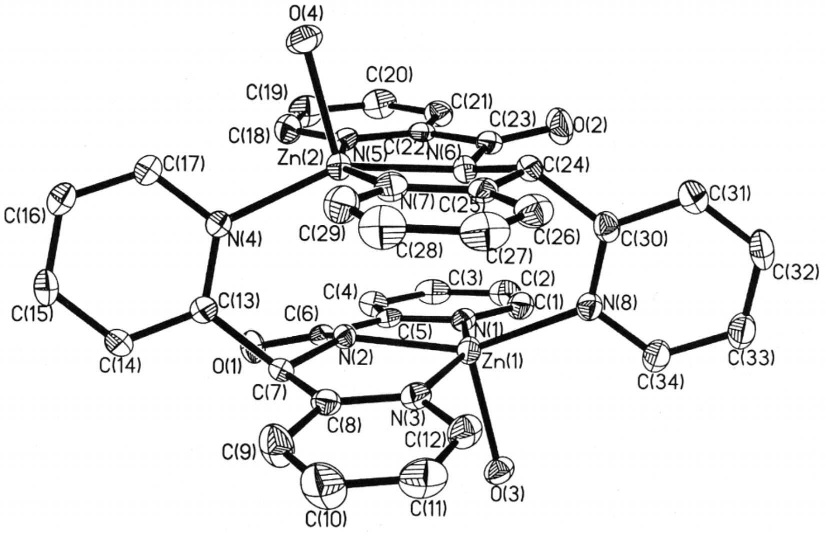


FIGURE 1 An ORTEP drawing of the cation $[ZnL(H_2O)]_2^{2+}$ showing the atom labeling scheme.

distances are 2.012(3) and 1.996(4) Å, respectively, longer than the corresponding copper(II)–N_{amido} distances [6]. Strong ligation by the axial water molecules is indicated by the Zn(II)–O distances of 2.050(3) Å [Zn(1)–O(3)] and 2.073(3) Å [Zn(2)–O(4)], respectively. Although dimerization of the [ZnL] units introduces significant strain in the cation, as evidenced by the small N(2)–Zn(1)–N(8) angle [153.26(14)°, Fig. 1], the complex is very stable both in air and in methanol. This abnormal stability can only be explained by the effects of ligand sharing. Minor π–π stacking between pyridine rings is noted in the cation, a fact that could provide some further stability to the dimeric structure. The zinc(II)–zinc(II) distance in the cation is 3.572 Å, longer than

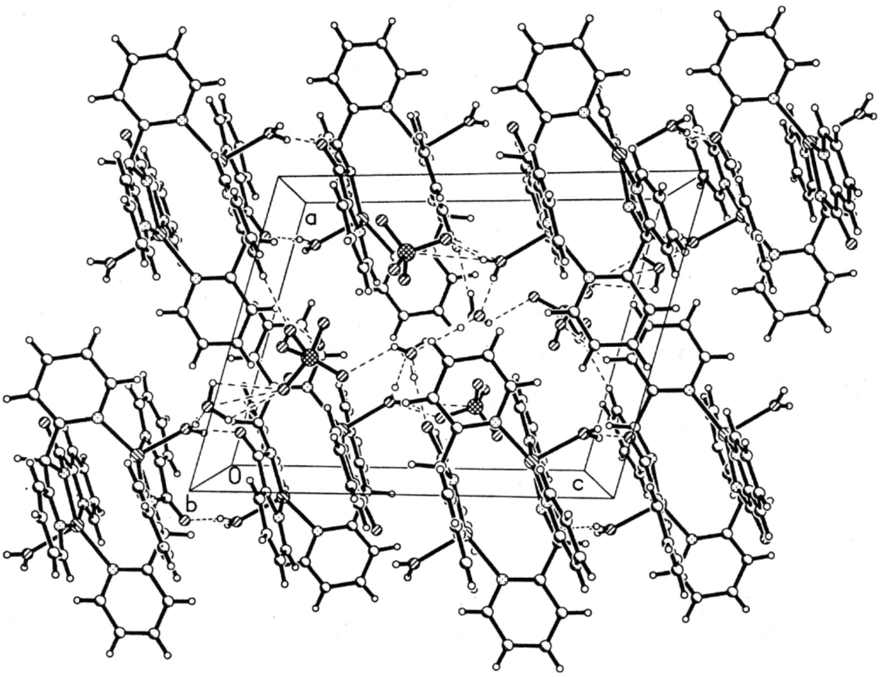


FIGURE 2 Packing diagram for the complex $[ZnL(H_2O)]_2(ClO_4)_2{\cdot}4H_2O$; a 2D network is formed by intermolecular hydrogen bonds.

the copper(II)–copper(II) distance (3.223 Å) [6], and the two zinc centers are not exactly coaxial (Fig. 1).

A sketch of intermolecular hydrogen bonds in the complex is shown in Fig. 2. An intermolecular hydrogen bond occurs between one oxygen atom of the carboxamide group and one hydrogen atom of the axial coordinated water of another unit ($D \cdots A = 1.797$ Å). The uncoordinated ClO_4^- anions and water molecules also form hydrogen bonds with the complex cations. Thus units of the complex are connected into a two-dimensional network structure (Fig. 2).

Spectral Properties

Coordination of carboxamido nitrogen to zinc(II) in the complex is evident from the red shift of the carbonyl stretching frequency (ν_{CO}) from 1669 cm^{-1} in the free ligand [11] to 1610 cm^{-1}. The N–H stretch of the free ligand (3352 cm^{-1}) is absent in IR spectra of the complex. Uncoordinated ClO_4^- anions give rise to a strong band at 1087 cm^{-1}.

Thermodynamic Properties

In order to investigate the thermodynamic stability of the dimeric complex in aqueous solution, we have studied the thermodynamic properties of the ligand with four bivalent metal ions, Co(II), Ni(II), Cu(II) and Zn(II). Protonation constants of the ligand were determined in aqueous solution by a potentiometric pH titration method described previously [12]. The experimental results suggest that this ligand has two stepwise protonation constants, pK_a 6.99 and 2.92, respectively, at 25°C. The two steps involve the two pyridine nitrogen atoms of the bis(2-pyridyl)methyl moiety. The pyridine nitrogen atom of the 2-pyridinecarboxamide moiety cannot be protonated in the pH range studied (2.5–11).

The potentially tetradentate ligand L with one carboxamido group and three pyridine arms is a good donor for metal ions. When the ligand is mixed with bivalent metal ions at a 1:1 ratio in solution, both monomeric compounds and dimeric moieties can be formed depending on the pH. In acid solution, because of the weak basicity of the pendant pyridine nitrogen, L can only act as a planar tridentate ligand with two pyridine and one carboxamido nitrogen atoms, to form two chelate rings with the metal centers; the pendant pyridine arm is uncoordinated. Thus monomeric compounds are the main species in solution. With increasing basicity of solution, two pendant pyridine arms of two neighboring [ZnL] units can coordinate to the other metal ion to form a dimer, as observed in the crystal structure. Although dimerization introduces significant strain in the complex, the dimer is greatly stabilized through ligand sharing and the dimers can dominate in basic solution. The stability constants of the complexes formed by the ligand with Co(II), Ni(II), Cu(II) and Zn(II) at a 1:1 ratio in aqueous solution are listed in Table III. The distribution curve for the Zn–L system is shown in Fig. 3.

The ligand can form three species with metal ions in solution, ML (110) (mononuclear complex), $M_2L_2H_{-2}$ (22–2) and $M_2L_2H_{-3}$ (22–3) (binuclear complexes), respectively. The species ML, $M_2L_2H_{-2}$ and $M_2L_2H_{-3}$ are formed at pH 4–9, 7–10 and >8, respectively, for the Zn–L system. The results show that the dimer is the main

TABLE III Stability constants of binary complexes of L with metal ions at 25°C

	CoL	NiL	CuL	ZnL
$\log\beta_{110}$	5.15 ± 0.04	5.55 ± 0.08	7.80 ± 0.07	5.33 ± 0.06
$\log\beta_{22\text{-}2}$	-3.61 ± 0.05	-3.02 ± 0.09	-0.13 ± 0.03	-2.95 ± 0.05
$\log\beta_{22\text{-}3}$	-14.43 ± 0.09	-14.24 ± 0.06	-10.59 ± 0.08	-11.56 ± 0.09

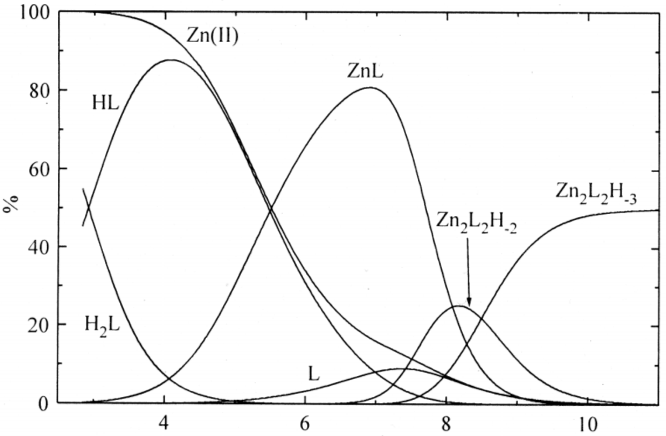


FIGURE 3 Species percentage distribution diagram as a function of pH for the Zn(II)–L system at 25°C.

species in basic solution and the species $M_2L_2H_{-2}$ (22–2) is the same as that in the crystal structure. We note that crystals were grown at pH 8–9. From Table III, it is apparent that the stability constant order is Co(II) < Ni(II) < Cu(II) > Zn(II), in agreement with the Irving–Williams series. For the dimeric complexes, the bond distances involving zinc(II) with the ligand are apparently longer than those of copper(II) ion (see above), which would also be consistent with the stability order.

Acknowledgments

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Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218507. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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