Pergamon

0277-5387(94)00269-X

Polyhedron Vol. 14, No. 4, pp. 511–514, 1995

0277-5387/95 $9.50+0.00

SYNTHESIS AND CRYSTAL STRUCTURE OF A BINUCLEAR ZINC(II) COMPLEX OF 2,6-DIFORMYLPYRIDINE *N*-OXIDE BIS(BENZOYLHYDRAZONE)

LI XIAOZENG,* WANG GENGLIN, LIAO DAIZHENG, YAN SHIPING
and JIANG ZONGHUI

Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China

and

WANG HONGGEN and YAO XINKAN

The Central Laboratory, Nankai University, Tianjin, 300071, P. R. China

(*Received* 29 *March* 1994; *accepted* 13 *July* 1994)

Abstract—The binuclear zinc(II) complex $[Zn_2L(O_2CCH_3)_2] \cdot CH_3CH_2OH$ was synthesized by a template reaction in alcohol. The crystal and molecular structure of this complex has been determined by X-ray analysis. The binucleating ligand L, 2,6-diformylpyridine *N*-oxide bis(benzoylhydrazone), is in doubly deprotonated form. All the coordinated atoms in the bis-Schiff base ligand and two zinc atoms in the complex molecule are coplanar, and the *N*-oxide oxygen atom bridges two zinc atoms with the same bond length of 2.24(1) Å. The two acetate ions act as bidentate ligands linking two zinc atoms, both being in a distorted trigonal-bipyramidal environment.

There have been many reports on binuclear complexes, but to our knowledge, few of them are on the bis-Schiff base ligands derived from 2,6-diformylpyridine *N*-oxide. This paper reports the synthesis, the crystal and molecular structure of a binuclear zinc complex of 2,6-diformylpyridine *N*-oxide bis(benzoylhydrazone) in doubly deprotonated form.

EXPERIMENTAL

Syntheses

2,6-Diformylpyridine *N*-oxide was synthesized according to the literature method.[1] Benzohydrazide was purchased from Shanghai Chemical Co.

$[Zn_2L(O_2CCH_3)_2] \cdot CH_3CH_2OH$. A solution of 0.5 mmol benzohydrazide in 10 cm^3 absolute alcohol was added to a solution of 0.25 mmol 2,6-diformylpyridine *N*-oxide and 0.5 mmol $Zn(O_2CCH_3)_2 \cdot 2H_2O$ in 20 cm^3 absolute alcohol. The reaction mixture was stirred at 60–70°C for 5 min. Then the stirring was continued at room temperature for 3 h. The resulting mixture was filtered, the yellow solid was washed with absolute alcohol and dried in air. Yield *ca* 65%. Found: C, 47.6; H, 4.0; N, 10.3. Calc. for $C_{27}H_{27}N_5O_8Zn_2$: C, 47.6; H, 3.7; N, 10.1%. This complex does not melt up to 300°C.

Elemental analyses were carried out using a Perkin–Elmer analyser model 240.

A needle-like yellow single crystal of $[Zn_2L(O_2CCH_3)_2] \cdot CH_3CH_2OH$ suitable for X-ray diffraction analysis was obtained by slow evaporation of a saturated absolute alcohol solution.

X-ray diffraction analysis

A single crystal sample of $[Zn_2L(O_2CCH_3)_2] \cdot CH_3CH_2OH$, having the approximate dimensions

---

* Author to whom correspondence should be addressed. Present address: Department of Chemistry, Tianjin University, Tianjin, 300072, P. R. China.

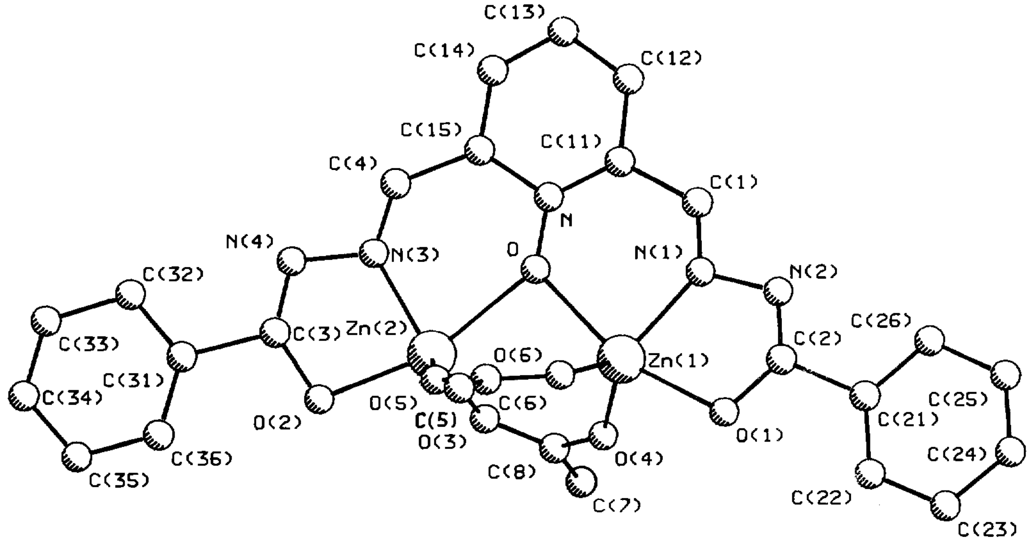

Fig. 1. The ORTEP drawing of $[Zn_2L(O_2CCH_3)_2]$ with the atom numbering scheme.

0.1 × 0.1 × 0.3 mm, was mounted on a glass fibre in a random orientation. The determination of the unit cell and data collection were performed with Mo-K_α radiation (λ = 0.7103 Å) on an Enraf–Nonius CAD-4 four-circle diffractometer equipped with a graphite crystal monochromater. A total of 3338 independent reflections were collected in the range $2 \leqslant \theta \leqslant 25°$ by the ω–2θ scan technique at room temperature, in which 916 reflections with $I \geqslant 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. The correction for LP factors was applied to the data.

The crystal structure is triclinic, space group $P\bar{1}$, with a = 10.173 (2) Å, b = 11.955 (6) Å, c = 13.422 (3) Å, α = 68.71 (3)°, β = 72.76 (2)°, γ = 73.31 (3)°, V = 1422.6 Å^3, M_r = 680.32, Z = 2, D_x = 1.59 g cm^{-3}, μ = 17.83 cm^{-1}, $F(000)$ = 694.

The structure was solved by direct methods, using the program MULTAN82. The zinc atoms were located from an E-map. The other non-hydrogen atoms were determined with successive difference Fourier syntheses. Hydrogen atoms were not found. The final refinement by full-matrix least-squares with anisotropic thermal parameters for zinc atoms and isotropic thermal parameters for the other non-hydrogen atoms was converged with unweighted and weighted agreement factors of 0.062 and 0.074. The highest peak on the final difference Fourier map was 0.45 e Å^{-3}.

All calculations were performed on a PDP11/44 computer using the SDP-PLUS program system.

RESULTS AND DISCUSSION

The ORTEP drawing of $[Zn_2L(O_2CCH_3)_2]$ with the atom numbering scheme is shown in Fig. 1.

Table 1. Selected bond lengths (Å) with estimated standard deviations

Zn(1)—O	2.24 (1)	Zn(2)—O	2.24 (1)
Zn(1)—O(1)	2.06 (2)	Zn(2)—O(2)	2.03 (1)
Zn(1)—O(4)	1.963 (9)	Zn(2)—O(3)	1.908 (9)
Zn(1)—O(6)	1.96 (1)	Zn(2)—O(5)	1.93 (1)
Zn(1)—N(1)	2.02 (1)	Zn(2)—N(3)	2.03 (1)
O(1)—C(2)	1.33 (2)	O(2)—C(3)	1.38 (2)
N(1)—N(2)	1.37 (2)	N(3)—N(4)	1.38 (3)
N(1)—C(1)	1.24 (3)	N(3)—C(4)	1.25 (3)
N(2)—C(2)	1.31 (2)	N(4)—C(3)	1.24 (3)
N—C(11)	1.33 (2)	N—C(15)	1.45 (2)
C(1)—C(11)	1.53 (2)	C(4)—C(15)	1.50 (2)
O—N	1.32 (1)		
O(4)—C(8)	1.31 (1)	O(3)—C(8)	1.29 (1)
O(6)—C(6)	1.27 (2)	O(5)—C(6)	1.28 (2)

Table 2. Selected bond angles (°) with estimated standard deviations

O—Zn(1)—O(1)	161.9 (4)	O—Zn(2)—O(2)	161.9 (4)
O—Zn(1)—O(4)	93.8 (4)	O—Zn(2)—O(3)	91.8 (4)
O—Zn(1)—O(6)	94.0 (4)	O—Zn(2)—O(5)	94.2 (5)
O—Zn(1)—N(1)	81.7 (5)	O—Zn(2)—N(3)	81.0 (5)
O(1)—Zn(1)—O(4)	95.5 (4)	O(2)—Zn(2)—O(3)	97.4 (4)
O(1)—Zn(1)—O(6)	95.6 (5)	O(2)—Zn(2)—O(5)	94.3 (5)
O(1)—Zn(1)—N(1)	80.3 (5)	O(2)—Zn(2)—N(3)	80.8 (5)
O(4)—Zn(1)—O(6)	117.2 (4)	O(3)—Zn(2)—O(5)	122.0 (4)
O(4)—Zn(1)—N(1)	114.6 (5)	O(3)—Zn(2)—N(3)	120.6 (5)
O(6)—Zn(1)—N(1)	128.1 (5)	O(5)—Zn(2)—N(3)	117.5 (5)
Zn(1)—O—N	129.9 (8)	Zn(2)—O—N	134.8 (9)
Zn(1)—O—Zn(2)	94.6 (4)		
O—N—C(11)	124 (1)	O—N—C(15)	117 (2)
O(3)—C(8)—O(4)	111.9 (9)	O(5)—C(6)—O(6)	119 (1)

Selected bond distances and angles with their estimated standard deviations are listed in Tables 1 and 2, respectively. The least-square plane through N(1), N(3), O, O(1), O(2), Zn(1) and Zn(2) is given in Table 3. The bis-Schiff base ligand L is pentadentate and the *N*-oxide oxygen acts as a bridging atom binding two zinc atoms. The distance between two zinc atoms is 3.29 (1) Å. Two acetate ions comprise two exogenous bridges. Each of the two zinc atoms are in a distorted trigonal-bipyramidal coordination environment. The deviation for Zn(1) from its equatorial plane through N(1), O(4) and O(6) is 0.011 (3) Å, while that of Zn(2) from its equatorial plane through N(3), O(3) and O(5) is 0.033(3) Å. All the bond angles in the equatorial planes depart only a little from 120°, with values ranging from 117.2 (4)° to 128.1 (5)°. The axes show comparatively large distortion from linearity, O—Zn(1)—O(1) and O—Zn(2)—O(2) both being 161.9(4)°. The two coordination polyhedra share *N*-oxide oxygen as one of their axial positions. The two zinc atoms both coordinated to the *N*-oxide oxygen with the same coordination bond length of 2.24(1) Å, which are the longest of all the coordination bonds in the complex. This may be considered a result of the comparatively weak coordination ability of the *N*-oxide oxygen atom.[2]

Table 3. The least-square plane through N(1), N(3), O, O(1), O(2), Zn(1) and Zn(2) and displacements (Å) of the atoms from the plane

Plane 1 : formed by Zn(1), N(1), O, N(3), Zn(2), O(1), O(2)
$0.195X+0.613Y-0.765Z-2.24 = 0$

Zn(1)	−0.082 (3)
N(1)	0.19 (2)
O	−0.05 (2)
N(3)	−0.13 (2)
Zn(2)	0.059 (3)
O(1)	−0.09 (2)
O(2)	0.10 (2)
Other atoms	
C(1)	0.26 (2)
C(2)	0.09 (2)
C(3)	−0.13 (2)
C(4)	−0.17 (2)
C(11)	0.16 (2)
C(15)	−0.05 (2)
N(2)	−0.26 (2)
N(4)	0.37 (2)

Table 3 shows that the five ligand atoms N(1), N(3), O, O(1) and O(2) provided by the bis-Schiff base ligand L, together with two zinc ions are coplanar (this plane is named plane 1). The dihedral angles between plane 1 and the benzene rings and the pyridine ring are not larger than 6(5)°. The whole bis-Schiff base ligand L in $[Zn_2L(O_2CCH_3)_2]$ has a tendency to planarity. The comparatively large deviations of some non-donor atoms in chelating rings from plane 1 may be caused by steric effects. The dihedral angles between plane 1 and the equatorial planes of the coordination polyhedra of Zn(1) and Zn(2) are 89.6(5)° and 86.3(4)°, respectively. The dihedral angle between the equatorial planes mentioned above is 69.3(6)°.

It can be seen from Table 1 that the bond lengths of carbonyls of the benzoyl hydrazide moities in the bis-Schiff base ligand L are larger than the typical length of C=O (1.23 Å),[3] and larger than the lengths of C—O bonds in the two acetate ion ligands in $[Zn_2L(O_2CCH_3)_2]\cdot CH_3CH_2OH$. The molecular structure shows that the species is a non-electrolyte and the ligand L must be the bideprotonated form of 2,6-diformylpyridine *N*-oxide bis(benzoylhydrazone).

Acknowledgement—This project was supported by the National Natural Science Foundation of China.

REFERENCES

1. D. Jerchel and J. Heider, *Ann. Bd.* 1958, **613**, 153.
2. N. M. Karayannis, A. N. Spaca, D. E. Chasan and L. L. Pytlewski, *Coord. Chem. Rev.* 1976, **20**, 37.
3. T. J. Giodano, G. J. Palenik, R. C. Palenik and D. A. Sullivan, *Inorg. Chem.* 1979, **18**, 2445.