

or high background(s); these reflections showed larger or smaller structure amplitudes than those of the equivalents. The deviations were up to several ten percent of the  $|F_o|$  values in most cases and several hundred percent in extreme cases for weak reflections. Such reflections were mainly concentrated in a limited region of the reciprocal lattice space, *i.e.*  $+h+k+l$  ( $\theta = 10^\circ \rightarrow 50^\circ$  and  $l = 10 \rightarrow 50$  depending on  $h$  and  $k$ ); after they were removed (695 in total), the equivalent reflections were averaged and used for the structure determination. Owing to the mechanical blind regions of the diffractometer, 574 high-angle reflections ( $62.5^\circ < \theta < 66^\circ$ ) could not be measured. The absorption correction was made by an analytical calculation using the crystal shape of the hexagonal plate. Water molecules were all isotropic. Large residual electron densities were not found in voids which could possibly contain some disordered water molecules.

In (2), the data collection was carried out first with an  $\omega$ -scan technique using  $\text{Cu } K\alpha$  radiation, and then with an  $\omega/2\theta$  scan using  $\text{Mo } K\alpha$  radiation, and finally some Bijvoet pairs were added to increase the number of reflections; thus, the effectiveness of the structure refinement gradually grew. The greatest problem, however, was the determination of the locations of the disordered anion near the (001) plane. A rigid group refinement was finally adopted for the positionally disordered anion formed by the B4, F13, F14, F15 and F16 atoms. In spite of prolonged calculations, the maximum  $\Delta/\sigma$  ratio was not less than 0.06. The  $y$  coordinate of the Co atom was fixed in the structure refinement. Water molecules were disordered at several sites. These and the disordered anions were refined isotropically. Large residual electron densities were not found in voids.

The absolute structure in each case was determined from about 100 selected Bijvoet pairs with large differences, by refinement of the inverted structure to significantly higher residuals, and by refinement of the Flack (1983) parameter.

For both compounds, data collection: *MSCIAFC Diffractometer Control System* (Rigaku Corporation, 1991); cell reduction: *MSCIAFC Diffractometer Control System*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1272). Services for accessing these data are described at the back of the journal.

## References

- Alcock, N. W. & Hough, E. (1972). *Acta Cryst.* **B28**, 1957–1960.
- Bernardo, K., Leppard, S., Robert, A., Commenges, G., Dahan, F. & Meunier, B. (1996). *Inorg. Chem.* **35**, 387–396.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Dickey, F. H., Fickett, W. & Lucas, H. L. (1952). *J. Am. Chem. Soc.* **74**, 944–951.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fukuda, T., Ishii, K., Nakano, Y. & Fujii, Y. (1997). Unpublished results.
- Jacobsen, E. N. (1993). *Catalytic Asymmetric Synthesis*, edited by I. Ojima, pp. 159–202. New York: VCH Publishers Inc.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Katsuki, T. (1995). *Coord. Chem. Rev.* **140**, 189–214.
- Lam, F., Xu, J. X. & Chan, K. S. (1996). *J. Org. Chem.* **61**, 8414–8418.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nagata, T., Yorozu, K., Yamada, T. & Mukaiyama, T. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2145–2147.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku Corporation (1991). *MSCIAFC Diffractometer Control System*. Rigaku Corporation, Tokyo, Japan.
- Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1999). **C55**, 1470–1472

## A maleate-bridged dinuclear bipyridine-containing zinc(II) complex

CUNGEN ZHANG,<sup>a</sup> KAIBEI YU,<sup>b</sup> DAN WU<sup>a</sup> AND CHENGXUE ZHAO<sup>a</sup>

<sup>a</sup>Chemistry Department, Shanghai Jiaotong University, Shanghai 200240, People's Republic of China, and <sup>b</sup>Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu 610041, People's Republic of China. E-mail: zcungen@kali.com.cn

(Received 14 January 1999; accepted 17 May 1999)

## Abstract

A novel cyclic dinuclear zinc complex with maleate dianions as the bridging ligands, di- $\mu$ -maleato-bis-[aqua(2,2'-bipyridine)zinc(II)] dihydrate,  $[\text{Zn}_2(\text{C}_4\text{H}_2\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , has been characterized by X-ray analysis. The complex lies about a crystallographic inversion centre. The zinc centre has distorted square-pyramidal geometry with two bipy N atoms, a carboxylate O atom and an aqua O atom forming the base; the Zn—N bond lengths are in the range 2.1021 (15)–2.120 (2) Å and the Zn—O bond lengths are in the range 1.9709 (13)–2.125 (2) Å. A maleate O atom completes the coordination sphere in the apical site, with a Zn—O bond length of 2.0223 (13) Å. The Zn···Zn distance is 5.281 (1) Å.

## Comment

Dinuclear zinc complexes with N- and O-donor ligands have been of considerable interest since such systems of two Zn atoms are known to exist at the active site of some zinc-containing enzymes, such as phospholipase

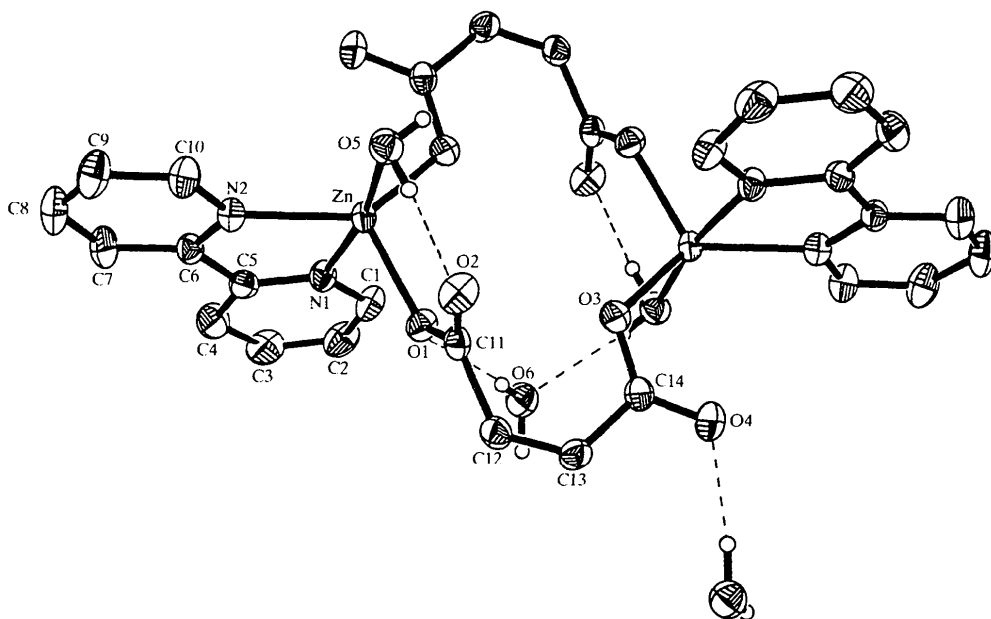
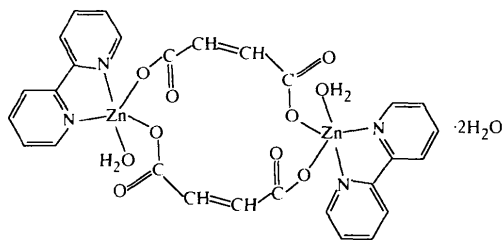


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

C (Huogh *et al.*, 1989) and bovine lens leucine aminopeptidase (Burley *et al.*, 1992). Several dinuclear zinc-carboxylate complexes have been synthesized and characterized structurally by X-ray diffraction (Uhlenbrock & Krebs, 1992; Chen *et al.*, 1994). We report here the crystal structure of a dinuclear zinc complex with maleate dianions as bridging ligands, (I).



(I)

The title compound forms centrosymmetric dinuclear molecules with maleate dianions acting as bridging ligands (Fig. 1). In the dinuclear molecule, two Zn atoms are linked by two maleate bridges forming a 14-membered non-planar macrocyclic structure. Each Zn atom in the complex is in a highly distorted square-pyramidal  $ZnO_3N_2$  coordination geometry. The Zn—N bond lengths of 2.1021(15) and 2.120(2) Å, respectively, are similar to those in  $[Zn_2(bipy)_2(MeCO_2)_3]ClO_4$  [2.127(5), 2.138(5), 2.100(5) and 2.151(5) Å; Chen *et al.*, 1994], but slightly longer than those in  $[Zn(bipy)Cl_2]$  [2.064(2) and 2.053(2) Å; Khan & Tuck, 1984]. The bite angle of 77.20(6)° is similar to those

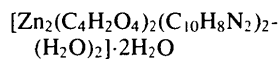
in  $[Zn_2(bipy)_2(MeCO_2)_3]ClO_4$  [77.1(2) and 76.8(2)°], but smaller than that in  $[Zn(bipy)Cl_2]$  [80.3(1)°].

The dinuclear molecules are linked to form an infinite chain by O—H...O hydrogen bonds; details are in Table 2.

## Experimental

To an aqueous solution of zinc sulfate (10 mmol, 20 ml) was added an aqueous solution of sodium maleate (10 mmol, 20 ml) with stirring for 30 min. To the colourless solution was added an ethanolic solution of bipy (10 mmol, 15 ml) with stirring. White solids precipitated immediately. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from the above filtrate.

### Crystal data



$M_r = 743.28$

Monoclinic

$C_2/c$

$a = 14.485(2) \text{ \AA}$

$b = 10.804(2) \text{ \AA}$

$c = 19.567(3) \text{ \AA}$

$\beta = 103.28(1)^\circ$

$V = 2980.3(8) \text{ \AA}^3$

$Z = 4$

$D_x = 1.657 \text{ Mg m}^{-3}$

$D_m = 1.66 \text{ Mg m}^{-3}$

$D_m$  measured by flotation  
in 1,2-dibromoethane and  
cyclohexane

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 29  
reflections

$\theta = 3.18\text{--}16.57^\circ$

$\mu = 1.681 \text{ mm}^{-1}$

$T = 290(2) \text{ K}$

Prism

$0.52 \times 0.44 \times 0.32 \text{ mm}$

Colourless

**Data collection**

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 semi-empirical  $\psi$  scans  
 (North *et al.*, 1968)  
 $T_{\min} = 0.529$ ,  $T_{\max} = 0.584$   
 3704 measured reflections  
 3269 independent reflections  
 2636 reflections with  
 $I > 2\sigma(I)$

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.025$   
 $wR(F^2) = 0.059$   
 $S = 1.057$   
 3268 reflections  
 225 parameters  
 H-atom parameters  
 constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$R_{\text{int}} = 0.012$   
 $\theta_{\max} = 27^\circ$   
 $h = 0 \rightarrow 18$   
 $k = 0 \rightarrow 13$   
 $l = -24 \rightarrow 24$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: 2.26%

$\Delta\rho_{\max} = 0.260 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.265 \text{ e } \text{\AA}^{-3}$   
 Extinction correction:  
 SHELXL93 (Sheldrick,  
 1993)  
 Extinction coefficient:  
 0.0054 (2)  
 Scattering factors from  
 International Tables for  
 Crystallography (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Zn—O3 <sup>i</sup>	1.9709 (13)	O1—C11	1.273 (2)
Zn—O1	2.0223 (13)	O2—C11	1.241 (2)
Zn—N2	2.1021 (15)	O3—C14	1.269 (2)
Zn—N1	2.120 (2)	O4—C14	1.239 (2)
Zn—O5	2.125 (2)		
O3 <sup>i</sup> —Zn—O1	108.85 (6)	N1—Zn—O5	170.06 (6)
O3 <sup>i</sup> —Zn—N2	134.92 (6)	C11—O1—Zn	127.98 (12)
O1—Zn—N2	115.35 (6)	C14—O3—Zn <sup>i</sup>	116.06 (12)
O3 <sup>i</sup> —Zn—N1	93.09 (6)	C5—N1—Zn	116.11 (12)
O1—Zn—N1	92.22 (5)	C1—N1—Zn	124.68 (13)
N2—Zn—N1	77.20 (6)	C10—N2—Zn	125.12 (13)
O3 <sup>i</sup> —Zn—O5	92.50 (7)	C6—N2—Zn	115.89 (12)
O1—Zn—O5	93.75 (6)	O2—C11—O1	126.2 (2)
N2—Zn—O5	93.05 (6)	O4—C14—O3	124.1 (2)

Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ .

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5A...O2	0.84	1.79	2.615 (2)	166
O5—H5B...O6 <sup>i</sup>	0.72	2.05	2.753 (3)	170
O6—H6A...O1	0.74	2.37	3.107 (3)	174
O6—H6B...O4 <sup>ii</sup>	0.84	1.94	2.774 (2)	173

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (ii)  $-x, -y, 1 - z$ .

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Data reduction: SHELXTL-Plus (Sheldrick, 1990a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990b). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

The work is supported by the Foundation of Shanghai Education Commission and Shanghai Jiaotong University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1534). Services for accessing these data are described at the back of the journal.

**References**

- Burley, S. K., David, P. R., Sweet, R. M., Taylor, A. & Lipscomb, W. N. (1992). *J. Mol. Biol.* **124**, 113–117.  
 Chen, X. M., Tong, Y. X. & Mak, T. C. W. (1994). *Inorg. Chem.* **33**, 4586–4588.  
 Huogh, E., Hansen, L. K., Birknes, B., Jynge, K., Hansen, S., Hardvick, A., Little, C., Dodson, E. & Derewenda, Z. (1989). *Nature*, **338**, 357–359.  
 Khan, M. A. & Tuck, D. G. (1984). *Acta Cryst.* **C40**, 60–62.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Sheldrick, G. M. (1990a). *SHELXTL-Plus. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1990b). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Uhlenbrock, S. & Krebs, B. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1451–1452.  
 Acta Cryst. (1999). **C55**, 1472–1475

## A dihomonuclear complex: di- $\mu$ -methacrylate-*O*:*O'*-bis[(1,10-phenanthroline-*N,N'*)bis(methacrylate-*O,O'*)ytterbium(III)]

WEIMIN LU, XIAOYANG LUO, BIN WU, JIANXIN MAO AND XIAOYUAN JIANG

Chemistry Department, Zhejiang University, Xixi Campus, Hangzhou 310028, People's Republic of China. E-mail: cuihua@tiger.hzuni.edu.cn

(Received 2 November 1998; accepted 18 May 1999)

**Abstract**

In the structure of the title complex, [Yb<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>O<sub>2</sub>)<sub>6</sub>-(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], each Yb<sup>3+</sup> ion is coordinated by six O atoms from four methacrylate ligands and by two N atoms of a phenanthroline ligand, giving a coordination polyhedron which is a distorted square antiprism. Within each centrosymmetric dinuclear molecule, two Yb<sup>3+</sup> ions are bridged by two bidentate bridging methacrylate ligands.

**Comment**

There is increasing interest in the stereochemistry of complexes of rare earth ions with unsaturated carboxylic acids because of the potential use of such complexes as extraction agents or as catalysts for hydrogenation, as well as the effect of the  $\alpha$ -C=C double bond on