

## METAL-ORGANIC COMPOUNDS

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**(Benzoato-*O*){tris[(2-benzimidazolyl)-*N*<sup>3</sup>-methyl]amine-*N*}zinc(II) Tetrafluoroborate Methanol Solvate**

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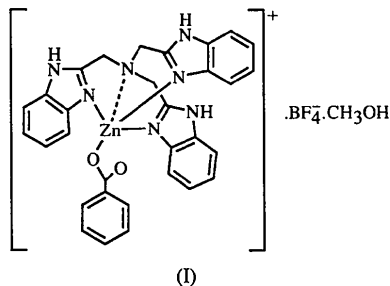
**Abstract**

In  $[LZn(C_6H_5CO_2)]BF_4 \cdot CH_3OH$  [ $L$  is tris(benzimidazolylmethyl)amine,  $C_{24}H_{21}N_7$ ], the ligand  $L$  is tetradentate ( $N_4$  donor set); the benzoate acts as a monodentate co-ligand and the methanol is not coordinated to the metal. The geometry at the zinc(II) centre is very close to trigonal bipyramidal.

**Comment**

As part of a study of the reactivity of zinc(II) complexes derived from tripodal and closely related ligands, we have shown recently that a dinuclear zinc(II) complex, derived from tris[(2-pyridinyl)methyl]amine, in which the metals are bridged by a phosphate monoester, can be readily synthesized (Adams *et al.*, 1995). Mononuclear zinc(II) complexes, derived from proligands composed of two pyridinyl and one phenolic arm have been shown to promote the hydrolysis of tris(4-nitrophenyl)-phosphate (Adams *et al.*, 1996). This paper presents the crystal structure of a mononuclear zinc(II) complex of the symmetrical tripodal ligand tris(benzimidazolylmethyl)amine ( $L$ ) (Thompson *et al.*, 1977) which has previously been used to synthesis a range of transition metal (Thompson *et al.*, 1978; Sakurai *et al.*, 1984) and zinc complexes (Thompson *et al.*, 1977; Gregorzik *et al.*, 1994; Hartmann *et al.*, 1994).

Crystals of  $[LZn(C_6H_5CO_2)]BF_4 \cdot CH_3OH$ , (I), contain discrete monomeric  $[LZn^{II}(C_6H_5CO_2)]^+$  cations,



methanol molecules and  $BF_4^-$  ions (Fig. 1 and Table 1). The coordination geometry at the Zn atom is distorted trigonal bipyramidal. Three imidazole N atoms (N1, N5, N7) from the pendant arms of the ligand form a trigonal plane; the Zn atom is displaced by 0.56 Å from this plane in the direction of the axial benzoate O1 atom. The bridgehead tertiary amine atom N3 is axially bonded to the Zn atom at a distance of 2.518 (4) Å and the Zn—O1 distance is 1.987 (3) Å. The benzoate O1 atom is almost collinear with the Zn atom and the bridgehead N3 atom [O1—Zn—N3 174.00 (13)°]. The non-bonding nature of the second carboxylate O atom is evident from the long Zn···O2 distance of 3.005 (4) Å. The benzoate group thus occupies the open axial site as a monodentate co-ligand and its presence inhibits the three benzimidazole moieties from forming a symmetric arrangement around the Zn atom [the three basal plane N—Zn—N angles are 105.0 (2), 107.8 (2) and 124.9 (2)°, respectively]. Bond angles and distances in the ligand are quite normal. The phenyl and imidazole rings are planar to within 0.03 Å. The dihedral angles between a phenyl ring and its corresponding imidazole ring are small: 4.7 (4), 2.4 (3) and 2.3 (3)°. The Zn atom lies in the planes of the imidazole rings; the deviations of Zn1 from the  $ZnC_3N_2$  planes are 0.032 (2), 0.077 (2) and 0.005 (2) Å for rings I, II and III, respectively. The  $BF_4$  anion is disordered over two sites, the refined site-occupancy factors being 0.48 (2) for B1, F1A, F2A, F3A and F4A, and 0.52 (2) for B1, F1B, F2B, F3B and F4B, with displacement parameters for some disordered F atoms showing marked anisotropy. The methanol of crystallization was

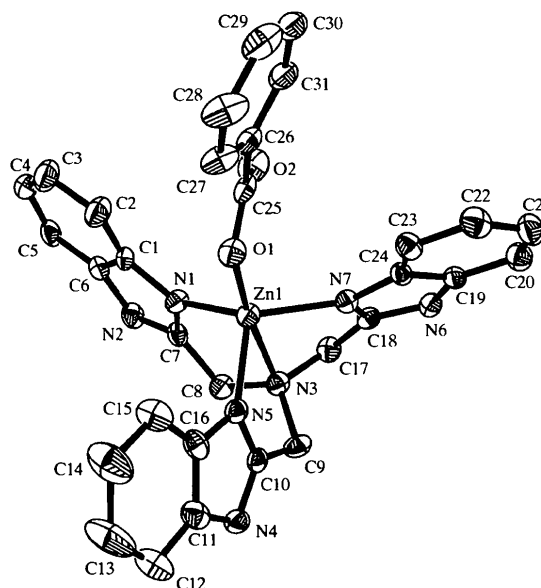


Fig. 1. The molecular structure of the  $[LZn(C_6H_5CO_2)]^+$  cation with atom labels and 50% probability ellipsoids (H atoms omitted).

also found to be disordered. An anisotropic model with occupancy over two sites produced no significant improvement in the model, at the expense of more parameters. The solvent was therefore modelled isotropically.

A residual peak of electron density ( $1.096 \text{ e } \text{\AA}^{-3}$ ) was found close to the disordered  $\text{BF}_4$  anion. The structure of a  $[\text{LZn}]$  complex with salicylate as the co-ligand and  $\text{ClO}_4^-$  as the counterion,  $[\text{LZn}(\text{OHC}_6\text{H}_4\text{COO})](\text{ClO}_4)$ , has been reported by Vahrenkamp and his co-workers (Hartmann *et al.*, 1994). The distorted trigonal bipyramidal geometry of the Zn atom in that complex is very similar to that found here and, as in the present complex, the co-ligand occupies the open axial site and is tightly bound, with a Zn—O distance of  $1.961 \text{ \AA}$ . The remaining bond lengths and angles are very similar to those reported here for  $[\text{LZn}(\text{C}_7\text{H}_5\text{O}_2)]\text{BF}_4$ .

## Experimental

$[\text{LZn}(\text{C}_6\text{H}_5\text{CO}_2)]\text{BF}_4 \cdot \text{CH}_3\text{OH}$  was prepared by heating a methanolic solution (45 ml) containing ligand (1 mmol, 0.41 g) and  $\text{Zn}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (1 mmol, 0.24 g) to reflux for 5 min; sodium benzoate (1 mmol, 0.14 g) in MeOH (5 ml) was added dropwise and reflux was continued for 2 h. The resulting solution was warm filtered and the filtrate left at room temperature overnight, whereupon single crystals deposited. When dried in a vacuum, the crystals lost solvent to produce a white powder. The microanalytical data listed below relate to the dry powder. Yield 0.40 g (55%). Elemental analysis (%) found (required for  $\text{C}_{31}\text{H}_{26}\text{N}_7\text{O}_2\text{BF}_4\text{Zn}$ ): C 54.27 (54.69), H 4.03 (3.85), N 14.35 (14.40). Selected IR bands (KBr disc): 1602 (C=N—Im), 1564 and 1387s (RCOO), 1083 ( $\text{BF}_4$ )  $\text{cm}^{-1}$ ; mass spectrum (+ve. FAB):  $m/z = 592$   $[\text{LZn}(\text{C}_6\text{H}_5\text{CO}_2)]^+$ , 471  $[\text{LZn}]^+$ , 100.

### Crystal data

|                                                                                                                          |                                           |
|--------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| $[\text{Zn}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{24}\text{H}_{21}\text{N}_7)]\text{BF}_4 \cdot \text{CH}_4\text{O}$ | Mo $K\alpha$ radiation                    |
| $M_r = 712.81$                                                                                                           | $\lambda = 0.71073 \text{ \AA}$           |
| Triclinic                                                                                                                | Cell parameters from 250 reflections      |
| $P1$                                                                                                                     | $\theta = 5\text{--}20^\circ$             |
| $a = 10.153(3) \text{ \AA}$                                                                                              | $\mu = 0.865 \text{ mm}^{-1}$             |
| $b = 12.228(3) \text{ \AA}$                                                                                              | $T = 293(2) \text{ K}$                    |
| $c = 14.166(3) \text{ \AA}$                                                                                              | Oblong block                              |
| $\alpha = 100.284(14)^\circ$                                                                                             | $0.60 \times 0.40 \times 0.30 \text{ mm}$ |
| $\beta = 98.644(11)^\circ$                                                                                               | Blue                                      |
| $\gamma = 112.866(10)^\circ$                                                                                             |                                           |
| $V = 1547.0(6) \text{ \AA}^3$                                                                                            |                                           |
| $Z = 2$                                                                                                                  |                                           |
| $D_x = 1.530 \text{ Mg m}^{-3}$                                                                                          |                                           |
| $D_m$ not measured                                                                                                       |                                           |

### Data collection

|                                                                    |                                        |
|--------------------------------------------------------------------|----------------------------------------|
| Delft Instruments FAST area detector with rotating anode generator | 3261 reflections with $I > 2\sigma(I)$ |
| Scanning procedure of Darr <i>et al.</i> (1993)                    | $R_{\text{int}} = 0.054$               |
| Absorption correction: none                                        | $\theta_{\text{max}} = 25.03^\circ$    |
| 6656 measured reflections                                          | $h = -11 \rightarrow 9$                |
| 4363 independent reflections                                       | $k = -14 \rightarrow 14$               |
|                                                                    | $l = -12 \rightarrow 15$               |

### Refinement

|                                         |                                                               |
|-----------------------------------------|---------------------------------------------------------------|
| Refinement on $F^2$                     | $(\Delta/\sigma)_{\text{max}} < 0.001$                        |
| $R[F^2 > 2\sigma(F^2)] = 0.057$         | $\Delta\rho_{\text{max}} = 1.096 \text{ e } \text{\AA}^{-3}$  |
| $wR(F^2) = 0.153$                       | $\Delta\rho_{\text{min}} = -0.867 \text{ e } \text{\AA}^{-3}$ |
| $S = 0.986$                             | Extinction correction: none                                   |
| 4362 reflections                        | Scattering factors from                                       |
| 461 parameters                          | International Tables for                                      |
| H atoms: see below                      | Crystallography (Vol. C)                                      |
| $w = 1/[\sigma^2(F_o^2) + (0.0873P)^2]$ |                                                               |
| where $P = (F_o^2 + 2F_c^2)/3$          |                                                               |

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

|           |             |           |             |
|-----------|-------------|-----------|-------------|
| Zn1—O1    | 1.987 (3)   | Zn1—N3    | 2.518 (4)   |
| Zn1—N5    | 2.013 (4)   | Zn1...O2  | 3.005 (4)   |
| Zn1—N1    | 2.031 (4)   | O1—C25    | 1.282 (6)   |
| Zn1—N7    | 2.052 (4)   |           |             |
| O1—Zn1—N5 | 107.8 (2)   | N1—Zn1—N7 | 124.9 (2)   |
| O1—Zn1—N1 | 109.0 (2)   | O1—Zn1—N3 | 174.00 (13) |
| N5—Zn1—N1 | 105.0 (2)   | N5—Zn1—N3 | 75.17 (15)  |
| O1—Zn1—N7 | 101.40 (14) | N1—Zn1—N3 | 74.68 (15)  |
| N5—Zn1—N7 | 107.8 (2)   | N7—Zn1—N3 | 72.63 (14)  |

H atoms were placed geometrically and subsequently rode on parent C or N atoms with  $U_{\text{iso}}$  equal to 1.2 (1.5 for methyl groups)  $U_{\text{eq}}$  of the carrier atom.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *REFINE* in *MADNES*. Data reduction: *ABSMAD* (Karaulov, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1311). Services for accessing these data are described at the back of the journal.

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