A Dinuclear Zinc Carboxylate Complex of Biological Relevance. Crystal Structure of [Zn₂(bpy)₂(MeCO₂)₃]ClO₄ (bpy = 2,2'-Bipyridine)

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Introduction

Dinuclear zinc complexes with N- and O-donor ligands are of current interest since such systems of two zinc atoms at distances less than 3.4 Å are known to exist at the active site of some zinc-containing enzymes, such as phospholipase C from *Bacillus cereus*[1] and bovine lens leucine aminopeptidase.[2] In the active site of the former enzyme, a pair of zinc atoms at a distance of 3.3 Å are bridged by a symmetric carboxylato-*O,O'* group and an OH⁻ or H₂O group. The active site of the latter enzyme contains a pair of zinc atoms at a distance of 2.91 Å, the structure has been refined at 2.35-Å resolution, and it has been suggested[2] that the dinuclear core is structurally analogous to that of myohemerythrin, which contains two μ-carboxylato-*O,O'* bridges and one μ-oxo bridge.[3] Recently, studies on small-molecular-weight model complexes indicated that the triple bridging system of the myohemerythrin type may have significantly larger metal–metal separation than 2.9 Å, and it was suggested that the pair of zinc atoms at a distance of 2.9 Å might be bridged by two symmetric monodentate carboxylato groups.[4]

Although zinc carboxylate complexes have been widely studied, dinuclear species containing carboxylato ligands are rare.[5] Hitherto four examples have been reported. These dinuclear structures feature μ-H₂O–μ-carboxylato-*O,O'*,[6] μ-hydroxy–bis(μ-carboxylato-*O,O'*),[4] tris(μ-carboxylato-*O,O'*),[7] or tetrakis(μ-carboxylato-*O,O'*) bridges.[8] Unfortunately, dinuclear zinc complexes linked by a pair of such monodentate carboxylato bridges have not yet structurally established. In this paper, we report a novel dinuclear zinc complex, [Zn₂(bpy)₂(MeCO₂)₃]-ClO₄ (1) (bpy = 2,2'-bipyridine), in which the two metal atoms

(1) Huogh, E.; Hansen, L. K.; Birknes, B.; Jynge, K.; Hansen, S.; Hardvick, A.; Little, C.; Dodson, E.; Derewenda, Z. *Nature* **1989**, *338*, 357.

(2) (a) Burley, S. K.; David, P. R.; Taylor, A.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 6878. (b) Burley, S. K.; David, P. R.; Sweet, R. M.; Taylor, A.; Lipscomb, W. N. *J. Mol. Biol.* **1992**, *124*, 113.

(3) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273.

(4) Chaudhuri, P.; Stockheim, C.; Wieghardt, K.; Deck, W.; Gregrozik, R.; Vahrenkamp, H.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1992**, *31*, 1451.

(5) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 925.

(6) Uhlenbrock, S.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1647.

(7) Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M. *Inorg. Chem.* **1984**, *23*, 1617.

(8) Clegg, W.; Little, I. R.; Straughan, S. P. *J. Chem. Soc., Dalton Trans.* **1986**, 1283.

Table 1. Crystallographic Data for **1**

chem formula	C₂₆H₂₅N₄ClO₁₀Zn₂
fw	719.69
a, Å	7.646(2)
b, Å	18.751(4)
c, Å	20.460(2)
β, deg	98.32(3)
V, Å³	2903(2)
Z	4
space group	*P*2₁/*n* (No. 14)
T, °C	21
ϱcalcd, g cm⁻³	1.647
ϱobsd, g cm⁻³	1.65
λ(Mo Kα), Å	0.710 73
*R*_F*ᵃ*	0.040
*R*_w*ᵇ*	0.047

ᵃ $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. ᵇ $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o) + 0.007|F_c|^2]^{-1}$.

are bridged by a pair of bidentate acetato-*O,O'* groups plus a monodentate acetato-*O* group.

Experimental Section

The C, H, and N microanalyses were carried out using a Perkin-Elmer 240Q elemental analyzer. FT-IR spectra were recorded (KBr pellets) with a Bio-Rad Digilab FTS-40 spectrometer. Densities of the crystals were measured by flotation in 1,2-dibromoethane/hexane.

Safty Note. Metal perchlorates containing organic ligands are potentially explosive. Only small amounts of material should be prepared and handled with great care.

Preparation. To a methanolic solution (20 mL) containing Zn-(MeCO₂)₂·2H₂O (0.22 g, 1.0 mmol) was added 2,2'-bipyridine (bpy) (0.178 g, 1.2 mmol). The mixture was stirred at room temperature for 30 min. Addition of NaClO₄ (0.2 g) in methanol (1 mL) and cooling of the resulting solution to 5 °C initiated the deposition of a colorless prismatic crystalline product within 1 week. The yield was 0.33 g (46%) of **1**. Anal. Calcd for C₂₆H₂₅N₄ClO₁₀Zn₂: C, 43.4; H, 3.5; N, 7.8. Found: C, 43.6; H, 3.5; N, 8.0. IR data (cm⁻¹): 3112 m, 3080 m, 3056 m, 3930 w, 2805 w, 1671 s, 1608 vs, 1599 vs, 1570 vs, 1492 s, 1477 vs, 1444 vs, 1420 vs, 1386 s, 1348 m, 1317 s, 1293 s, 1252 m, 1224 w, 1181 m, 1161 s, 1095 vs, 1100–1062 vs, br, 1024 s, 981 m, 976 m, 904 w, 815 w, 771 vs, 736 s, 684 m, 670 m, 654 s, 623 vs, 416 m.

X-ray Crystallography. A selected single crystal of **1** was used to collected X-ray data at 392 K on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å). Cell parameters were obtained by a least-squares fit from the setting of 25 well-centered reflections with 12 ≤ 2θ ≤ 23°. A total of 5560 reflections were measured with the variable-speed ω-scan technique (3 ≤ 2θ ≤ 50°), of which 2609 unique data were observed with *I* ≥ 3σ(*I*) and were used in the refinement. Crystallographic data are summarized in Table 1. Data processing, absorption, solution, and full-matrix least-squares refinement were performed with the SHELXTL-PC program package.[9] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically (C–H = 0.96 Å) with isotropic thermal parameters and included in the final stage of structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[10] The atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are tabulated in Table 2, and selected bond lengths and angles are given in Table 3; lists of the remaining bond lengths and angles, hydrogen atom coordinates, and anisotropic thermal parameters are available as supplementary material.

(9) Sheldrick, G. M. *SHELXTL-PC, Program Package for X-ray Crystal Structure Determination*; Siemens Analytical X-ray Instruments, Inc.: Karlsruhe, Germany, 1990.

(10) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birminghan, England, 1974; Vol. 5, pp 55, 99, 149.

Table 2. Atomic Coordinates ($\times 10^5$ for Zn, $\times 10^4$ for Others) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^4$ for Zn, $\text{Å}^2 \times 10^3$ for Others) for **1**

	x	y	z	$U(\text{eq})^a$
Zn(1)	13262(10)	3730(4)	16821(3)	554(3)
Zn(2)	17878(9)	21080(3)	16403(3)	519(3)
O(1)	3501(6)	653(2)	2356(2)	70(2)
O(2)	3894(5)	1839(2)	2298(2)	61(2)
C(1)	4322(8)	1222(3)	2521(3)	56(2)
C(2)	5974(9)	1170(3)	3022(4)	90(3)
O(3)	2603(7)	540(2)	895(2)	93(2)
O(4)	2743(6)	1729(2)	827(2)	71(2)
C(3)	3004(9)	1106(4)	629(3)	66(3)
C(4)	3909(10)	1032(4)	18(3)	86(3)
O(5)	31(6)	1310(2)	1671(2)	57(2)
O(6)	−2126(8)	688(3)	1172(4)	140(3)
C(5)	−1583(12)	1274(4)	1395(4)	79(3)
C(6)	−2666(10)	1927(4)	1293(4)	99(4)
N(11)	318(6)	−187(2)	2462(2)	51(2)
N(12)	819(6)	−669(3)	1283(3)	55(2)
C(10)	94(8)	107(3)	3049(3)	60(2)
C(11)	−510(8)	−294(4)	3544(3)	64(3)
C(12)	−833(8)	−1012(4)	3442(3)	63(3)
C(13)	−560(8)	−1313(3)	2848(3)	60(2)
C(14)	8(8)	−884(3)	2366(3)	49(2)
C(15)	289(8)	−1161(3)	1700(3)	51(2)
C(16)	47(9)	−1862(3)	1517(3)	67(3)
C(17)	341(9)	−2083(4)	888(4)	77(3)
C(18)	846(10)	−1578(4)	460(3)	75(3)
C(19)	1070(9)	−886(4)	674(3)	68(3)
N(21)	1574(6)	3113(2)	1179(2)	51(2)
N(22)	758(6)	2771(2)	2358(2)	54(2)
C(20)	1983(9)	3259(3)	573(3)	63(3)
C(21)	1867(9)	3931(3)	300(3)	70(3)
C(22)	1298(9)	4485(3)	664(4)	73(3)
C(23)	860(9)	4341(3)	1285(3)	63(3)
C(24)	986(8)	3656(3)	1524(3)	48(2)
C(25)	583(7)	3468(3)	2203(3)	49(2)
C(26)	116(8)	3967(3)	2650(3)	57(2)
C(27)	−234(9)	3735(4)	3262(3)	70(3)
C(28)	−69(9)	3024(4)	3420(3)	70(3)
C(29)	432(9)	2555(4)	2965(3)	71(3)
Cl(1)	1436(3)	1397(1)	4599(1)	75(1)
O(7)	1420(8)	768(3)	4983(2)	101(2)
O(8)	1863(11)	1981(4)	4998(3)	159(4)
O(9)	−311(9)	1492(4)	4216(3)	137(3)
O(10)	2653(8)	1325(3)	4128(3)	104(2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Complex **1** comprises a discrete dinuclear $[Zn_2(bpy)_2(MeCO_2)_3]^+$ cation and a perchlorate anion. As shown in Figure 1, in the dinuclear cation, a pair of zinc atoms at a distance of 3.275(2) Å are linked by a pair of symmetric μ-acetato-O,O' bridges (Zn—O = 2.006(4)−2.066(4) Å) and a symmetric μ-acetato-O bridge (Zn—O = 2.013(4), 2.010(4) Å). The triply-bridged dinuclear cation of **1** represents a new coordination geometry in dizinc chemistry, to be contrasted with the known μ-OH−bis(μ-carboxylato-O,O') and tris(μ-carboxylato-O,O') systems.[4,6] Analogous structures have been established for [Fe$_2$-(HCO)$_4$(BIPhMe)$_2$] (BIPhMe = bis(1-methylimidazol-2-yl)-phenylmethoxymethane)[11] and [Cu(bpy)$_2$(MeCO$_2$)$_3$]ClO$_4$.[12] Each zinc atom in **1** is in a highly distorted trigonal-bipyramidal ZnO$_3$N$_2$ coordination geometry with the axial positions being occupied by O(3) and N(11), with O(3)—Zn(1)—N(11) at

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg)

Zn(1)—O(1)	2.066(4)	Zn(1)—O(3)	2.018(6)
Zn(1)—O(5)	2.010(4)	Zn(1)—N(11)	2.138(5)
Zn(1)—N(12)	2.127(5)	Zn(2)—O(2)	2.006(4)
Zn(2)—O(4)	2.033(5)	Zn(2)—O(5)	2.013(4)
Zn(2)—N(21)	2.100(5)	Zn(2)—N(22)	2.151(5)
O(1)—C(1)	1.257(8)	O(2)—C(1)	1.265(8)
C(1)—C(2)	1.509(9)	O(3)—C(3)	1.248(9)
O(4)—C(3)	1.259(8)	C(3)—C(4)	1.515(10)
O(5)—C(5)	1.281(10)	O(6)—C(5)	1.236(10)
C(5)—C(6)	1.473(11)		

O(1)—Zn(1)—O(3)	93.4(2)	O(1)—Zn(1)—O(5)	97.6(2)
O(3)—Zn(1)—O(5)	98.5(2)	O(1)—Zn(1)—N(11)	88.2(2)
O(3)—Zn(1)—N(11)	159.1(2)	O(5)—Zn(1)—N(11)	102.0(2)
O(1)—Zn(1)—N(12)	124.9(2)	O(3)—Zn(1)—N(12)	85.3(2)
O(5)—Zn(1)—N(12)	137.1(2)	N(11)—Zn(1)—N(12)	76.8(2)
O(2)—Zn(2)—O(4)	96.6(2)	O(2)—Zn(2)—O(5)	105.4(2)
O(4)—Zn(2)—O(5)	94.8(2)	O(2)—Zn(2)—N(21)	122.0(2)
O(4)—Zn(2)—N(21)	87.7(2)	O(5)—Zn(2)—N(21)	132.0(2)
O(2)—Zn(2)—N(22)	91.4(2)	O(4)—Zn(2)—N(22)	164.8(2)
O(5)—Zn(2)—N(22)	95.7(2)	N(21)—Zn(2)—N(22)	77.1(2)
Zn(1)—O(1)—C(1)	135.7(4)	Zn(2)—O(2)—C(1)	127.7(4)
Zn(1)—O(3)—C(3)	130.8(5)	Zn(2)—O(4)—C(3)	132.5(4)
Zn(1)—O(5)—Zn(2)	108.6(2)	Zn(1)—O(5)—C(5)	113.5(4)
Zn(2)—O(5)—C(5)	128.9(4)	Zn(1)—N(11)—C(10)	124.5(4)
Zn(1)—N(11)—C(14)	116.3(4)	Zn(1)—N(12)—C(15)	115.9(4)
Zn(1)—N(12)—C(19)	126.0(4)	Zn(2)—N(21)—C(20)	125.5(4)
Zn(2)—N(21)—C(24)	116.8(4)	Zn(2)—N(22)—C(25)	115.7(4)
Zn(2)—N(22)—C(29)	125.5(4)	O(1)—C(1)—O(2)	125.6(5)
O(1)—C(1)—C(2)	117.6(5)	O(2)—C(1)—C(2)	116.8(5)
O(3)—C(3)—O(4)	126.0(6)	O(3)—C(3)—C(4)	116.6(6)
O(4)—C(3)—C(4)	117.4(6)	O(5)—C(5)—O(6)	117.4(7)
O(5)—C(5)—C(6)	120.2(6)	O(6)—C(5)—C(6)	122.2(7)
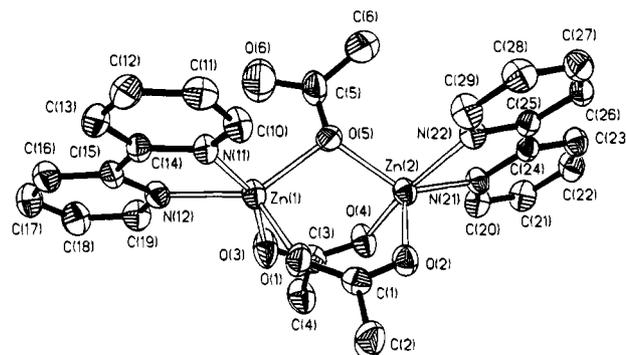
Figure 1. ORTEP plot showing the structure of the dinuclear cation in **1** and the atom-numbering scheme.

159.1(2)° for Zn(1), and by O(4) and N(22), with O(4)—Zn-(2)—N(22) at 164.8(2)° for Zn(2). The mean Zn—O bond length (2.04 Å) in **1** is slightly shorter than the corresponding value (2.08 Å) found for a dinuclear complex with the zinc atoms in six-coordination[4] and slightly longer than that found for a dinuclear unit with the zinc atoms in four coordination (1.95 Å).[6] These results suggest that the metal—ligand bond lengths should be shortened with the decrease of coordination number.

The most interesting finding in **1** is the symmetric mono-dentate acetato bridge, which is seldom observed in metal carboxylates.[5] Complex **1** exhibits the following important carboxylate IR absorption bands: $\nu_{as}(CO_2)$ at 1671 s and 1599 vs and $\nu_{sym}(CO_2)$ at 1444 vs and 1420 vs cm^{-1}. The two separations (Δ) between $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ are 251 and 155 cm^{-1}, in which the larger and smaller Δ values can be

(11) Tolman, W. B.; Bino, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 8522. Tolman, W. B.; Liu, S.; Benten, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 152.

(12) Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 3657.

(13) Deacon, G. B.; Philips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(14) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 3, p 435.

correlated to the monodentate and bidentate acetato groups, respectively.[13,14]

The present study provides the first example of a dinuclear zinc complex containing a monodentate carboxylato bridge and, more importantly, gives circumstantial evidence for the proposed model that the pair of zinc atoms at an unusually short Zn···Zn distance (2.9 Å) in the active site of the leucine aminopeptidase may be achieved by a pair of symmetric monodentate carboxylato bridges.[4] The Zn···Zn separation can be considerably shortened by the presence of a monodentate carboxylato group in the triply-bridged dinuclear cation of **1** (3.275 Å) in comparison with that found in a tris(μ-carboxylato-O,O')-bridged dinuclear zinc complex (3.54 Å).[7] It is also notable that dinuclear zinc complexes with metal—metal separations shorter than 3.0 Å are found in the complexes containing bis(μ-hydroxo) bridges,[15,16] which are analogous to the monodentate μ-carboxylato-O bridges. A presumably shorter metal—metal distance than 3.0 Å may be possible in the bis(μ-carboxylato-O)-bridged dizinc core.

It is somewhat surprising that, in the recently reported crystal structure of the leucine aminopeptidase, only one *syn-syn* μ-carboxylato-O,O' bridge (Glu334) in the dizinc active site has been structurally established at 2.35-Å resolution.[2b] In contrast, in a well-structurally characterized zinc-containing enzyme[1] and a model complex,[6] a pair of zinc atoms bridged by a similar μ-carboxylato-O,O' bridge plus a μ-oxo(hydroxo, aqua) bridge are separated at a distance significantly larger than 3.0 Å. The metal—metal distance in a dinuclear core is primarily dictated by the nature of the bridging system, and insertion of additional bridging ligands tends to reduce the metal—metal separation.[4] These facts imply that a *single* μ-carboxylato-O,O' might be of difficulty to bring two zinc atoms at the unusually short distance of 2.9 Å in the native leucine aminopeptidase, especially in the case that the flexibility of the active site has been confirmed by the binding of the inhibitor bestatin to the active site, which resulted in a remarked increase of the metal—metal separation to 3.12 Å and no significant conformational changes.[2b] Therefore further studies of the crystal structure of this enzyme at a higher resolution as well as related small-molecular-weight model complexes may be necessary to understand what governs the unusually short metal—metal separation.

Supplementary Material Available: Tables of crystallographic parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atomic coordinates and thermal parameters and a figure showing the unit cell (5 pages). Ordering information is given on any current masthead page.

(15) Al-Juaid, S. S.; Buttrus, H. N.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 909.

(16) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Koschmieder, S. U. *J. Chem. Soc., Chem. Commun.* **1987**, 1319.