oxygenases, e.g. pterin-dependent copper phenylalanine hydroxylase and dopamine β-hydroxylase, which appear to utilize mononuclear copper centers in activation of O_2 by copper ions.

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Supplementary Material Available: A full table of crystal data (Table VI) and listings of bond lengths (Table VIII), bond angles (Table IX), anisotropic temperature factors (Table X), and hydrogen coordinates and temperature factors (Table XI) for **4a**$(ClO_4)_2$ and figures showing UV-vis spectra, vacuum cycling, and carbonyl cycling (11 pages); a listing of observed and calculated structure factors (Table VII) (32 pages). Ordering information is given on any current masthead page.

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Mono- and Dinuclear Zinc(II) Complexes of Biological Relevance. Crystal Structures of $[L_2Zn](PF_6)_2$, $[L'Zn(O_2CPh)_2(H_2O)]$, $[L'_2Zn_2(\mu\text{-}OH)_2](ClO_4)_2$, and $[L'_2Zn_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2](ClO_4)\cdot H_2O$ (L = 1,4,7-Triazacyclononane, L′ = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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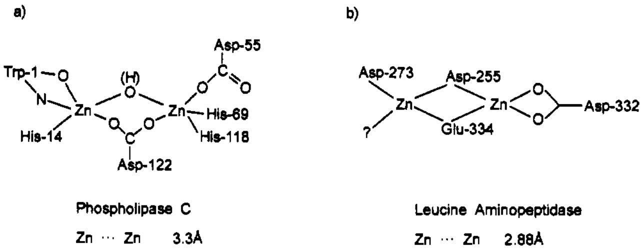
The macrocycle 1,4,7-triazacyclononane ($C_6H_{15}N_3$; L) reacts with Zn(II) ions in methanolic solution forming the 2:1 species $[L_2Zn]^{2+}$. The crystal structure of $[L_2Zn](PF_6)_2$ (**1**) has been determined. Crystal data: space group $C2/c$, a = 9.719 (2) Å, b = 16.312 (3) Å, c = 15.017 (3) Å, β = 92.04 (3)°, V = 2379.3 (8) Å^3, and Z = 4. The zinc ions are in a distorted octahedral environment of six amine nitrogen donor atoms. In contrast, the sterically more demanding tridentate macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane ($C_9H_{21}N_3$; L′) forms 1:1 species containing the L′Zn fragment. In the presence of sodium benzoate the mononuclear species $[L'Zn(O_2CPh)_2(H_2O)]$ (**2**) is generated. Crystal data: space group $P\bar{1}$, a = 8.193 (2) Å, b = 12.173 (2) Å, c = 13.387 (3) Å, α = 79.53 (3)°, β = 72.48 (3)°, γ = 70.93 (3)°, V = 1198.2 (4) Å^3, and Z = 2. The Zn(II) ions are in a distorted octahedral environment composed of three facially coordinated amine nitrogen, two carboxylate oxygen atoms, and a water molecule. The two carbonyl oxygen atoms of the carboxylato groups are intramolecularly hydrogen bonded to the coordinated water molecule. In aqueous solution in the absence of coordinating ligands the L′Zn fragment was found to generate the di-μ-hydroxo-bridged dinuclear species $[L'_2Zn_2(\mu\text{-}OH)_2](ClO_4)_2$ (**3**). Crystal data: space group $P2_1/n$, a = 8.703 (2) Å, b = 8.325 (2) Å, c = 20.470 (4) Å, β = 90.96 (3)°, V = 1482.9 (6) Å^3, and Z = 2. The Zn(II) ions are in a distorted square base pyramidal environment (five-coordinate). In the presence of excess sodium acetate L′Zn fragments form the dinuclear species $[L'_2Zn_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2](ClO_4)\cdot H_2O$ (**4**). Crystal data: space group $P4_12_12$, a = 10.90 (1) Å, c = 27.86 (1) Å, V = 3310.0 (10) Å^3, and Z = 4. The dinuclear cation contains the (μ-hydroxo)bis(μ-acetato)dizinc(II) core and two tridentate macrocyclic capping ligands. Both zinc ions are in an octahedral ligand environment. Complexes **3** and **4** serve as structural models for the spatial arrangement of the two zinc(II) ions in the active sites of the enzymes phospholipase C from *Bacillus Cereus* and leucine aminopeptidase from bovine lens, respectively.

Introduction

The synthesis and structural characterization of classical Werner-type coordination compounds of zinc(II) with N- and O-donor ligands has in the past few years experienced a dramatic resurgence.[2] This is undoubtedly triggered by the rapidly growing knowledge of the structures of zinc-containing active sites of a variety of enzymes. While the majority of these appear to contain one zinc(II) ion in their respective active site,[3] there have recently been reported the structures of two enzymes which contain two zinc ions in close proximity (<3.4 Å) in the respective active site.[4,5] In the enzyme phospholipase C from *Bacillus cereus* there are three zinc(II) ions per subunit, two of which are at a distance of 3.3 Å. These two are connected by one symmetrical carboxylate bridge (Asp 122) and a bridging OH^- or H_2O group. All three metal ions are approximately trigonal bipyramidal. The ligand environment of the dinuclear part is shown schematically in Chart Ia. In contrast, bovine lens leucine aminopeptidase contains two zinc(II) ions at a distance of only 2.88 Å. Since the structure of this enzyme has been refined at 2.7 Å resolution, the exact nature of the first coordination spheres around the zinc ions has not been fully established. A sketch is shown in Chart Ib. Most importantly from our perspective, no single atom bridging groups H_2O or OH^- have been identified which could account for the rather short Zn···Zn distance. Aspartate-255 and glutamate-334 are suggested to form two carboxylate bridges. It is our aim to provide circumstantial evidence from low-molecular-weight model complexes how the two zinc ions can be forced at this close distance.

Chart I



Phospholipase C
Zn ··· Zn 3.3Å

Leucine Aminopeptidase
Zn ··· Zn 2.88Å

Lacking ligand field stabilization energy, zinc(II) exhibits no preferential, electronically favored coordination number, and consequently, four-, five-, and six-coordinate complexes are most

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† Deceased.

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0020-1669/92/1331-1451$03.00/0

Table I. Crystallographic Data for Complexes

	complex			
	1	**2**	**3**	**4**
chem formula	$(C_6H_{15}N_3)_2Zn(PF_6)_2$	$C_{23}H_{33}N_3O_5Zn$	$C_{18}H_{44}Cl_2N_6O_{10}Zn_2$	$C_{22}H_{51}N_6O_{10}ClZn_2$
fw	613.7	496.9	706.2	725.9
space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P4_12_12$
a, Å	9.719 (2)	8.193 (2)	8.703 (2)	10.90 (1)
b, Å	16.312 (3)	12.173 (2)	8.325 (2)	
c, Å	15.017 (3)	13.387 (3)	20.470 (4)	27.86 (1)
α, deg		79.53 (3)		
β, deg	92.04 (3)	72.48 (3)	90.96 (3)	
γ, deg		70.93 (3)		
V, Å^3	2379.3 (8)	1198.2 (4)	1482.9 (6)	3310.0 (10)
Z	4	2	2	4
T, °C	22	22	22	22
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.713	1.377	1.582	1.45
μ(Mo Kα), nm^{-1}	1.292	1.084	1.895	1.62
R^a	0.058	0.050	0.044	0.059
$R_w{}^b$	0.054	0.057	0.044	0.064

$^a R = ||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum_w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w^{-1} = \sigma^2(F) + 99.000F^2$.

abundant[1] but three-coordinate[6] species may also be obtained by using sterically demanding ligands. Subtle steric effects appear to dictate the actual polyhedra in zinc(II) complexes. For instance, the ring size of cyclic triaza macrocycles appears to be important. In [{Zn([12]aneN$_3$)OH}$_3$](ClO$_4$)$_3$·HClO$_4$, where [12]aneN$_3$ is 1,5,9-triazacyclododecane, the zinc is in a slightly distorted tetrahedral environment.[7] Similarly, the pendent arm derivative 1-(3-(dimethylamino)propyl)-1,5,9-triazacyclododecane has recently been shown to form a tetrahedral ZnN$_4$ polyhedron.[8] The chelating N–Zn–N bond angles average 104.8°, which are close to the ideal tetrahedral angle of 109.5°. In complexes containing the smaller macrocycle 1,4,7-triazacyclononane (L) the chelating N–M–N angles are usually 70–80°; i.e., they are significantly smaller than the tetrahedral angle. They are closer to the octahedral angle of 90°.[11] Consequently, zinc(II) ions form the stable octahedral 2:1 complex [L$_2$Zn]$^{2+}$.[9,10] We here report the crystal structure of [L$_2$Zn](PF$_6$)$_2$ with this ligand.

The tripodal amine ligand tris((methylamino)methyl)ethane, forms tetrahedral 1:1 complexes LZnX$_2$ where only two amine nitrogen atoms are coordinated or an octahedral 2:1 complex with all six amine groups coordinated.[12] 1:1 complexes of 1,4,7-triazacyclononane (L) and its N-methylated derivative L′ with zinc(II) do not show this complication; all three amine nitrogens are always bound to the zinc ion.

The L′Zn fragment may bind additional ligands forming mononuclear or dinuclear species. Of special interest to us were species containing carboxylate and/or hydroxo bridging ligands. Two dinuclear complexes, namely [L′Zn(μ-OH)$_2$ZnL′](ClO$_4$)$_2$ and [L′$_2$Zn$_2$(μ-OH)(μ-CH$_3$CO$_2$)$_2$](ClO$_4$)·H$_2$O, have been synthesized and structurally characterized.

Experimental Section

The ligands 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) were prepared according to published procedures.[13] All other chemicals were obtained from commercial sources and used without further purification.

Preparation of Complexes. [L$_2$Zn](PF$_6$)$_2$ (1). To a solution of Zn(ClO$_4$)$_2$·6H$_2$O (0.37 g; 1 mmol) in methanol (15 mL) was added 1,4,7-triazacyclononane (0.30 g; 2.3 mmol) at ambient temperature with stirring. Within 1 h in a colorless microcrystalline precipitate of [L$_2$Zn](ClO$_4$)$_2$ formed, which was collected by filtration (yield: 0.40 g; 77%). A 0.25-g amount of this material was dissolved in water (10 mL), and solid NaPF$_6$ (0.12 g; 1.0 mmol) was added. From the clear solution colorless crystals of the hexafluorophosphate salt precipitated within 3 d. The crystals were found to be suitable for a single-crystal X-ray structure determination.

Anal. Calcd for (C$_6$H$_{15}$N$_3$)$_2$Zn(PF$_6$)$_2$ (mol wt 613.7): C, 23.48; H, 4.93; N, 13.69. Found: C, 23.6; H, 5.1; N, 13.7.

[L′Zn(O$_2$CPh)$_2$(H$_2$O)] (2). To a solution of ZnCl$_2$ (0.14 g, 1.0 mmol) in a water/acetonitrile mixture (1:1; 10 mL) was added 1,4,7-trimethyl-1,4,7-triazacyclononane (0.20 g; 1.2 mmol) and sodium benzoate (0.28 g; 2.0 mmol). The solution was heated to 50 °C for 1 h. After standing for 12 h at ambient temperature, colorless crystals formed, which were collected by filtration (yield: 0.30 g; ≈50%).

Anal. Calcd for C$_{23}$H$_{33}$N$_3$O$_5$Zn (mol wt 496.9): C, 55.59; H, 6.69; N, 8.46. Found: C, 55.4; H, 6.7; N, 8.3.

[L′$_2$Zn$_2$(μ-OH)$_2$](ClO$_4$)$_2$ (3). To a solution of Zn(ClO$_4$)$_2$·6H$_2$O (0.37 g; 1.0 mmol) in water (10 mL) was added 1,4,7-trimethyl-1,4,7-triazacyclononane (0.20 g; 1.2 mmol). The solution was gently heated to 40 °C for 30 min. Upon cooling of the mixture to 5 °C, a colorless, microcrystalline precipitate formed, which was recrystallized from a water/methanol mixture (1:1) (yield: 0.21 g; 60%).

Anal. Calcd for C$_{18}$H$_{44}$N$_6$O$_{10}$Cl$_2$Zn$_2$ (mol wt 706.2): C, 30.61; H, 6.28; N, 11.90. Found: C, 31.0; H, 6.2; N, 11.7.

[L′$_2$Zn$_2$(μ-OH)(μ-CH$_3$CO$_2$)$_2$](ClO$_4$)·H$_2$O (4). To a solution of Zn(CH$_3$CO$_2$)$_2$·2H$_2$O (0.22 g; 1.0 mmol) in methanol (30 mL) was added 1,4,7-trimethyl-1,4,7-triazacyclononane (0.20 g; 1.2 mmol). The clear solution was stirred at room temperature for 30 min. Addition of NaClO$_4$·H$_2$O (0.40 g) and cooling to 0 °C initiated the precipitation of colorless crystals within 24 h, which were collected by filtration (yield: 0.45 g; 60%).

Anal. Calcd for C$_{22}$H$_{51}$N$_6$O$_{10}$Cl$_2$Zn$_2$ (mol wt 725.9): C, 36.41; H, 7.08; N, 11.58; ClO$_4$, 13.71; Zn, 18.01. Found: C, 36.3; H, 7.0; N, 11.4; ClO$_4$, 13.8; Zn, 18.2.

X-ray Crystallography. Crystal data, data collection, and refinement are summarized in Table I. Colorless crystals of **1**–**4** were mounted on a glass fiber and placed on an Enraf-Nonius CAD 4 or AED II (Siemens) diffractometer. Graphite-monochromated Mo Kα X-radiation was used throughout. Unit cell parameters were determined by the automatic indexing of 35 centered reflections. Intensity data were corrected for Lorentz and polarization effects. Only for **4** an absorption correction was deemed to be necessary and carried out (empirical; ψ-scans of light reflections in the range $6 \leq 2\theta \leq 50°$). The structures were solved by direct (**1**–**3**) and Patterson and difference Fourier methods (**4**) by using the SHELXTL-PLUS program package.[14] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for **1**

	x	y	z	U(eq)^a
Zn	7500	2500	0	38 (1)
N(1)	7002 (7)	2981 (3)	−1332 (3)	76 (2)
N(2)	9073 (5)	3438 (3)	−70 (5)	79 (3)
N(3)	6323 (5)	3565 (3)	350 (3)	59 (2)
C(1)	8493 (10)	3285 (5)	−1605 (5)	102 (4)
C(2)	9163 (8)	3773 (6)	−905 (7)	111 (4)
C(3)	8575 (9)	4069 (4)	624 (6)	97 (4)
C(4)	7179 (10)	4257 (4)	529 (5)	91 (4)
C(5)	5352 (7)	3676 (6)	−448 (6)	106 (4)
C(6)	5977 (11)	3603 (5)	−1290 (6)	119 (4)
P	2581 (2)	3616 (1)	1556 (1)	61 (1)
F(1)	3825 (4)	4233 (3)	1397 (3)	98 (2)
F(2)	3516 (5)	2898 (3)	1254 (3)	108 (2)
F(3)	1339 (4)	3020 (3)	1727 (3)	115 (2)
F(4)	2053 (5)	3763 (4)	570 (3)	120 (2)
F(5)	3131 (5)	3483 (3)	2551 (3)	104 (2)
F(6)	1684 (5)	4361 (3)	1868 (4)	120 (2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for **2**

	x	y	z	U(eq)^a
Zn(1)	252 (1)	3090 (1)	2979 (1)	32 (1)
N(1)	−166 (6)	3085 (4)	1425 (3)	37 (2)
N(2)	−1577 (7)	1969 (4)	3419 (4)	49 (2)
N(3)	−2362 (6)	4461 (4)	3128 (3)	45 (2)
O(1)	2512 (5)	1676 (3)	2646 (3)	46 (2)
O(2)	3118 (5)	1176 (4)	4211 (3)	57 (2)
O(3)	1615 (5)	4331 (3)	2371 (3)	45 (2)
O(4)	1829 (6)	4786 (4)	3862 (3)	58 (2)
O(5)	324 (5)	3042 (4)	4544 (3)	42 (2)
C(1)	−819 (12)	2096 (8)	1499 (6)	83 (4)
C(2)	−1459 (18)	1567 (9)	2446 (7)	126 (7)
C(3)	−3347 (10)	2736 (9)	3879 (9)	116 (5)
C(4)	−3696 (10)	3892 (9)	3752 (9)	105 (5)
C(5)	−2558 (15)	4825 (8)	2068 (6)	122 (5)
C(6)	−1430 (10)	4196 (7)	1256 (5)	81 (4)
C(7)	1551 (8)	2980 (6)	596 (4)	54 (3)
C(8)	−1063 (10)	992 (6)	4182 (5)	64 (3)
C(9)	−2493 (9)	5460 (5)	3643 (5)	59 (3)
C(10)	3436 (7)	1084 (5)	3265 (5)	41 (2)
C(11)	5134 (7)	169 (5)	2773 (4)	39 (2)
C(12)	5783 (8)	190 (5)	1691 (5)	52 (3)
C(13)	7368 (9)	−604 (7)	1242 (6)	70 (3)
C(14)	8310 (10)	−1416 (6)	1891 (7)	74 (4)
C(15)	7689 (9)	−1454 (6)	2950 (6)	64 (3)
C(16)	6093 (8)	−658 (5)	3402 (5)	47 (3)
C(17)	1963 (7)	4947 (5)	2901 (4)	41 (2)
C(18)	2603 (7)	5961 (5)	2301 (4)	38 (2)
C(19)	3212 (8)	6046 (6)	1206 (4)	49 (3)
C(20)	3802 (9)	6987 (7)	675 (5)	64 (3)
C(21)	3810 (10)	7836 (6)	1208 (6)	69 (4)
C(22)	3192 (10)	7773 (6)	2282 (6)	65 (3)
C(23)	2610 (8)	6843 (5)	2833 (5)	49 (3)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

correction for non-hydrogen atoms were taken from ref 15. The positions of the hydrogen atoms of the methylene and methyl groups and of the N-H groups in **1** were placed at calculated positions with group isotropic thermal parameters, while the methyl groups were treated as rigid bodies, each with three rotational variables. All non-hydrogen atoms were refined with anisotropic thermal parameters. Tables II-V give the final coordinates for **1-4**, respectively.

Results

Zompa et al.[9] and Kimura et al.[10] have found from potentiometric titrations that 1,4,7-triazacyclononane and zinc(II) ions form a very stable 1:1 complex in aqueous solution. They have not prepared the corresponding 2:1 complex. This species is formed readily in a methanolic solution of the ligand and Zn(ClO_4)$_2$·6H_2O (2:1). The colorless perchlorate salt [ZnL_2](ClO_4)$_2$ has been isolated as a microcrystalline solid. The corresponding

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for **3**

	x	y	z	U(eq)^a
Zn	5173 (1)	781 (1)	4338 (1)	38 (1)
O	4067 (4)	−1016 (5)	4761 (2)	66 (2)
N(1)	6810 (4)	2420 (5)	3878 (2)	47 (2)
N(2)	4895 (5)	−18 (5)	3334 (2)	50 (2)
N(3)	3548 (5)	2534 (5)	4069 (2)	46 (1)
C(11)	8323 (7)	2496 (10)	4198 (4)	87 (3)
C(22)	4664 (9)	−1761 (8)	3263 (4)	91 (3)
C(33)	2514 (7)	2897 (8)	4617 (3)	73 (3)
C(1)	6911 (9)	1984 (10)	3189 (3)	95 (3)
C(2)	6306 (7)	464 (9)	2997 (3)	72 (3)
C(3)	3519 (6)	865 (9)	3076 (3)	69 (2)
C(4)	2640 (7)	1726 (9)	3548 (3)	79 (3)
C(5)	4362 (7)	3961 (7)	3849 (4)	83 (3)
C(6)	6005 (7)	3938 (8)	3950 (4)	92 (3)
Cl	52 (2)	7537 (2)	3721 (1)	59 (1)
O(1)	206 (5)	8555 (6)	3168 (2)	77 (2)
O(2)	−1471 (6)	7147 (9)	3801 (3)	142 (3)
O(3)	598 (9)	8301 (10)	4270 (3)	173 (4)
O(4)	862 (11)	6165 (10)	3605 (4)	205 (5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å$^2 \times 10^3$) for **4**

atom	x	y	z	U^a
Zn(1)	1661 (1)	−104 (1)	4661 (1)	38 (1)*
O(1)	1502 (4)	1502 (4)	5000	35 (2)*
O(2)	1391 (5)	−1152 (5)	5276 (2)	51 (2)*
O(3)	−162 (5)	−237 (5)	4443 (2)	49 (2)*
N(1)	1979 (6)	−1841 (6)	4226 (2)	45 (3)*
N(2)	2272 (6)	653 (6)	3960 (2)	50 (3)*
N(3)	3693 (6)	−299 (6)	4737 (3)	54 (3)*
C(1)	1683 (9)	−1452 (8)	3733 (3)	56 (3)*
C(2)	2362 (8)	−311 (8)	3588 (2)	65 (4)*
C(3)	3471 (9)	1204 (8)	4086 (3)	81 (5)*
C(4)	4326 (8)	344 (10)	4348 (3)	72 (4)*
C(5)	3888 (7)	−1645 (8)	4713 (3)	75 (4)*
C(6)	3274 (8)	−2247 (8)	4268 (3)	72 (4)*
C(7)	1151 (9)	−2836 (7)	4365 (3)	72 (4)*
C(8)	1420 (8)	1651 (10)	3782 (3)	75 (5)*
C(9)	4095 (7)	167 (10)	5194 (3)	69 (4)*
C(10)	499 (7)	−1035 (7)	5550 (3)	42 (3)*
C(11)	265 (9)	−2070 (8)	5915 (4)	85 (5)*
Cl(1)	5627 (3)	5627 (3)	0	84 (1)*
Wa(1)	2340 (11)	2340 (11)	0	253 (8)*
O(11)	6676 (16)	4908 (19)	152 (5)	133 (5)
O(12)	4797 (18)	4908 (18)	221 (5)	135 (7)
O(13)	6025 (16)	6633 (19)	219 (7)	168 (9)
O(14)	5439 (21)	5062 (20)	459 (8)	169 (9)

^{a} An asterisk indicates an equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

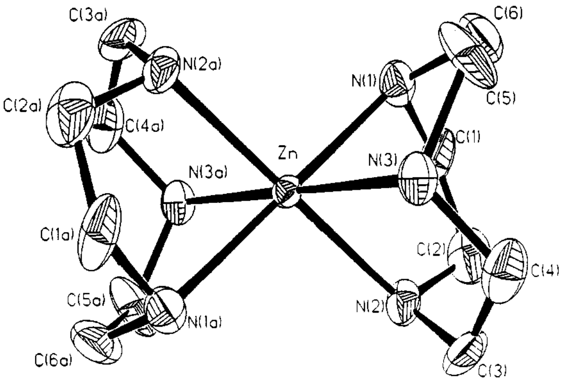

Figure 1. Structure of the dication in crystals of **1**.

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Table VI. Selected Bond Distances (Å) and Angles (deg) of Complexes **1**–**4**

		1	
Zn–N(1)	2.187 (5)	Zn–N(3)	2.156 (5)
Zn–N(2)	2.168 (5)		
N(1)–Zn–N(2)	80.6 (2)	N(1)–Zn–N(3)	80.3 (2)
N(2)–Zn–N(3)	79.9 (2)	N(1)–Zn–N(1a)	180.0 (1)
N(2)–Zn–N(1a)	99.4 (2)	N(3)–Zn–N(1a)	99.7 (2)
		2	
Zn–N(1)	2.210 (5)	Zn–O(5)	2.103 (4)
Zn–N(2)	2.228 (6)	O(2)···O(5)	2.64 (1)
Zn–N(3)	2.222 (4)	O(4)–C(17)	1.241 (7)
O(4)···O(5)	2.68 (1)	O(3)–C(17)	1.266 (9)
Zn–O(1)	2.071 (3)	O(2)–C(10)	1.233 (8)
Zn–O(3)	2.074 (5)	O(1)–C(10)	1.258 (7)
N(1)–Zn–N(2)	80.1 (2)	N(1)–Zn–N(3)	80.4 (2)
N(2)–Zn–N(3)	80.2 (2)	N(1)–Zn–O(1)	89.6 (2)
N(2)–Zn–O(1)	92.7 (2)	N(3)–Zn–O(1)	168.6 (2)
N(1)–Zn–O(3)	90.7 (2)	N(2)–Zn–O(3)	168.2 (2)
N(3)–Zn–O(3)	91.0 (2)	O(1)–Zn–O(3)	94.7 (2)
N(1)–Zn–O(5)	172.4 (2)	N(2)–Zn–O(5)	92.9 (2)
N(3)–Zn–O(5)	95.5 (2)	O(1)–Zn–O(5)	93.7 (2)
O(3)–Zn–O(5)	95.7 (2)		
		3	
Zn–O(1)	1.986 (4)	Zn–N(3)	2.099 (4)
Zn–N(1)	2.197 (4)	Zn–O(a)	1.957 (4)
Zn–N(2)	2.170 (5)	Zn···Zn(a)	3.024 (1)
O(1)–Zn–N(1)	167.9 (2)	O(1)–Zn–N(3)	108.0 (2)
N(1)–Zn–N(2)	81.2 (2)	N(2)–Zn–N(3)	84.3 (2)
N(1)–Zn–N(3)	83.9 (2)	N(1)–Zn–O(1a)	97.5 (2)
O(1)–Zn–O(1a)	79.8 (2)	N(3)–Zn–O(1a)	113.2 (2)
N(2)–Zn–O(1a)	162.4 (2)	Zn–O(1)–Zn(a)	100.2 (2)
O(1)–Zn–N(2)	97.7 (2)		
		4	
Zn(1)–O(1)	1.996 (4)	Zn(1)–O(2)	2.080 (5)
Zn(1)–O(3)	2.084 (5)	Zn(1)–N(1)	2.275 (7)
Zn(1)–N(2)	2.222 (6)	Zn(1)–N(3)	2.236 (6)
O(2)–C(10)	1.242 (10)	O(3)–C(10a)	1.244 (9)
Zn(1)···Zn(1a)	3.311 (2)		
O(1)–Zn(1)–O(2)	94.6 (2)	O(1)–Zn(1)–O(3)	96.7 (2)
O(2)–Zn(1)–O(3)	93.9 (2)	O(1)–Zn(1)–N(1)	174.3 (2)
O(2)–Zn(1)–N(1)	90.2 (2)	O(3)–Zn(1)–N(1)	86.1 (2)
O(1)–Zn(1)–N(2)	96.6 (2)	O(2)–Zn(1)–N(2)	166.0 (2)
O(3)–Zn(1)–N(2)	93.2 (2)	N(1)–Zn(1)–N(2)	78.2 (2)
O(1)–Zn(1)–N(3)	97.2 (2)	O(2)–Zn(1)–N(3)	90.6 (2)
O(3)–Zn(1)–N(3)	165.1 (2)	N(1)–Zn(1)–N(3)	79.7 (2)
N(2)–Zn(1)–N(3)	79.7 (3)	Zn(1)–O(1)–Zn(1a)	112.1 (3)

hexafluorophosphate has been obtained from an aqueous solution of the perchlorate salt by addition of $NaPF_6$.

Figure 1 shows the structure of the dication in crystals of **1**; Table VI summarizes important bond distances and angles. The zinc ion is in a pseudooctahedral all-nitrogen environment. Due to the steric constraints of the nine-membered ring, the intraligand N–Zn–N angles are significantly smaller (average 80.3°) than the ideal octahedral angle of 90°. This has been observed for all structurally characterized $[L_2M]^{n+}$ complexes.[11]

The average Zn–N distance at 2.17 is quite long and agrees well with Sargeson's cage complex $[Zn(di(AmH)scar)](NO_3)_4$ (di(AmH)sar = 1,8-diammonio-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)[16] with an average Zn–N distance of 2.19 ± 0.12 Å. The long Zn–N distances in **1** may be enforced by interligand H···H repulsions, as was analyzed by Hancock et al.[17] In $[ZnL^1_2](ClO_4)_2$ (L^1 = $CH_3C(CH_2NHCH_3)_3$, tris((methylamino)methyl)ethane), which also contains a ZnN_6 octahedron of secondary amine nitrogens, the average Zn–N distance is found at 2.213 (4) Å.[12] In contrast, in two zinc complexes with a tetrahedral ligand environment comprised of a twelve-membered macrocycle such as 1,5,9-triazacyclododecane and a pendent arm derivative thereof[18] the Zn–N distances are considerably shorter at 2.002 and 2.00 Å, respectively.

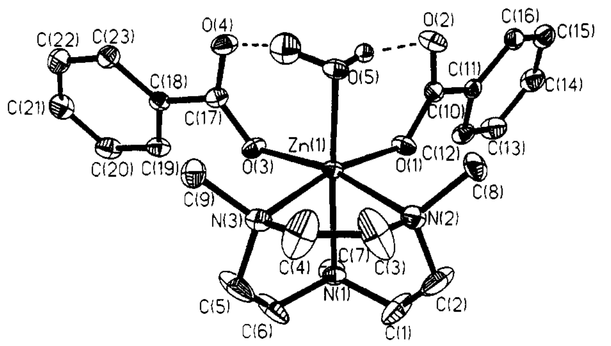

Figure 2. Structure of the neutral molecule in crystals of **2**.

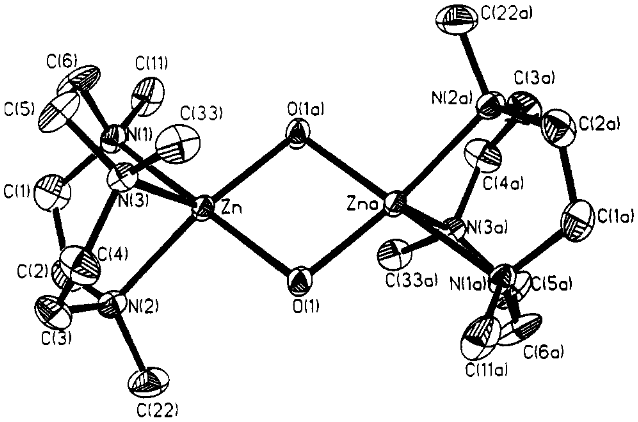

Figure 3. Structure of the dication in crystals of **3**.

Reaction of $ZnCl_2$ with 1,4,7-trimethyl-1,4,7-triazacyclononane and sodium benzoate in the ratio 1:1:2 in a water/acetonitrile mixture (1:1) results in the formation of colorless crystals of $[L'Zn(O_2CPh)_2(H_2O)]$ (**2**). In the infrared spectrum (KBr disk) of **2** the ν_{as}(C–O) and ν_s(C–O) stretching frequencies are observed at 1608 and 1393 cm^{-1}, respectively. The difference of 215 cm^{-1} between the two is indicative of monodentate carboxylates. A broad, nearly featureless absorption between 3400 and 2400 cm^{-1} is typical for extensively hydrogen-bonded water molecules. Both structural features are clearly identified in the structure of **2**. Figure 2 displays a perspective view of the neutral molecule; Table VI gives selected bond distances and angles. The zinc ion is in pseudooctahedral environment which is comprised of three facially bound tertiary nitrogen atoms of the macrocyclic amine, two oxygen atoms—one of each carboxylate group of benzoate—and one coordinated water molecule (N_3O_3 donor set). The hydrogen atoms of the water molecule have been located in the difference Fourier map and were included in fixed positions in the last cycle of the refinement. The most interesting feature of this complex is the presence of *two* intramolecular hydrogen bonding contacts between the carbonyl oxygen atoms O(4) and O(5) and the coordinated water molecule: O(4)···O(5) at 2.68 Å and O(2)···O(5) at 2.64 Å. Kennard et al.[19] have observed a similar intramolecular hydrogen bond in $[Zn(H_2O)_4(2,4\text{-}D)_2]$ (D = (2,4-dichlorophenoxy)acetato), where one uncomplexed carboxylate oxygen is tied into the complex by an intramolecular hydrogen bond to a water ligand.

Reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ and 1,4,7-trimethyl-1,4,7-triazacyclononane (1:1.2) in water at 30 °C affords colorless crystals of $[L'_2Zn_2(\mu\text{-}OH)_2](ClO_4)_2$ (**3**) in 60% yield. A sharp absorption maximum at 3650 cm^{-1} in the infrared spectrum (KBr disk) is

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Table VII. Survey of Structures of Zinc Complexes with Oxygen (H_2O, OH^-, OR^-) and Carboxylate Bridges[a]

	Zn···Zn, Å	CN[b]	ref
(A) Singly Bridges Species			
$[L''_6Zn_2(\mu\text{-}OH)](ClO_4)_3$	3.54	4	*c*
(B) Doubly Bridged Species			
$[L'_2Zn_2(\mu\text{-}OH)_2](ClO_4)_2$ (**3**)	3.02	5	this work
$[L^2_2Zn_2Cl_2]$	3.245	5	*d*
$[(Tpsi)_2Zn_2(\mu\text{-}OH)_2]$	2.96	3	*e*
$[Zn_2(t\text{-}Bu_2P)_2(OH)(\mu\text{-}OH)]_2$	2.71	4	*f*
$[Fe_2(TPA)_2(\mu\text{-}O)(\mu\text{-}OBz)](ClO_4)_3\cdot 2H_2O$	3.24	6	*g*
$[L^3Zn_2(\mu\text{-}OBz)(OH_2)](ClO_4)_2\cdot 2H_2O\cdot 2CH_3OH$	3.443	6, 5	29
(C) Triply Bridged Species			
$[L'_2Zn_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2](ClO_4)\cdot H_2O$ (**4**)	3.31	6	this work
$[FeZn(BMP)(\mu\text{-}CH_3CO_2)_2][BPh_4]_2$	3.44	6	*h*
$[Zn_3(crot)_6(C_9H_7N)_2]$	3.26	4, 6, 4	*i*
$[Zn_2(\mu\text{-}CH_3CO_2)_3][Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]\cdot 2H_2O$	3.54	4	*j*
(D) Quadruply Bridged Species			
$[Zn_2(crot)_4(C_9H_7N)_2]$	2.98	5	*i*
$[Zn_2(\mu\text{-}hyxan)(SO_4)(\mu\text{-}H_2O)_2(H_2O)_2]$	~3.1	6	*k*

[a] Abbreviations of ligands: L″ = 3-*tert*-butylpyrazole; L^2 = 4-methyl-2,6-bis(pyrazolyl-1-methyl)phenolate; Tpsi = tris(dimethylphenylsilyl)methyl; TPA = tris(2-pyridylmethyl)amine; BMP = 2,6-bis[((bis(2-pyridylmethyl)amino)methyl)]-4-methylphenolate; C_9H_7N = quinoline; crot = crotonate; OBz = benzoate; hyxan = hypoxanthine; L^3 = 2,6-bis[bis((2-benzimidazolylmethyl)amino)methyl]-4-methylphenolate. [b] CN = coordination number. [c] Alsfasser, R.; Powell, A. K.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 938. [d] Chen, C.-T.; Chang, W.-K.; Shen, S. C.; Lee, G.-H.; Ho, T.-I.; Lin, Y.-C.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1991**, 1569. [e] Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 909. [f] Arif, A. M.; Cowley, A. H.; Jones, R. A.; Koschmieder, S. U. *J. Chem. Soc., Chem. Commun.* **1987**, 1319. [g] Norman, R. E.; Yan, S.; Que, L., Jr.; Backes, G.; Ling, J.; Sanders-Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*. 1554. [h] Borovik, A. S.; Que, L., Jr.; Papaefthymiou, V.; Münck, E.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 1986. [i] Clegg, W.; Little, I. E.; Straughan, B. P. *J. Chem. Soc., Dalton Trans.* **1986**, 1283. [j] Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M. *Inorg. Chem.* **1984**, *23*, 1617. [k] Dubler, E.; Hänggi, G.; Schmalle, H. *Inorg. Chem.* **1990**, *29*, 2518.

indicative of μ-hydroxo bridges which are not involved in hydrogen bonding to other acceptor groups. Figure 3 displays the structure of the dication, and Table VI summarizes selected bond distances and angles. Each zinc ion in the dinuclear dication is in a distorted square based pyramidal environment of three nitrogen atoms of the macrocycle (two in basal and one in apical positions) and two oxygen atoms of two μ-hydroxo bridges. The proton of the hydroxo bridge has been located in the final difference Fourier map. The dication possesses crystallographic symmetry C_i. **3** is isostructural and isomorphous with the previously reported copper complex $[L'_2Cu_2(\mu\text{-}OH)_2](ClO_4)_2$.[20] Interestingly, the apical Zn–N(3) bond distance in **3** is shorter than the two basal Zn–N distances whereas in the corresponding copper complex the reverse is observed. This reflects the usual difference between an open-shell d^9 and a closed-shell d^{10} electronic configuration. The nonbonding Zn···Zn distance in **3** is at 3.024 (1) Å; the Zn–O–Zn bond angle is obtuse at 100.2 (2)° whereas the O–Zn–O angle is acute at 79.8 (2)°. This is typical for the bis(μ-hydroxo)dimetal core without direct metal–metal bonding.

When a methanolic solution of $Zn(CH_3CO_2)_2\cdot H_2O$ and 1,4,7-trimethyl-1,4,7-triazacyclononane (1:1.2) was treated with $NaClO_4\cdot H_2O$, colorless crystals of $[L'_2Zn_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2](ClO_4)\cdot H_2O$ (**4**) precipitated out within 24 h at 0 °C. The infrared spectrum (KBr disk) exhibits a sharp (OH) stretching frequency at 3668 cm^{-1} and the ν_{as}(C–O) and ν_s(CO) stretching frequencies of bridging carboxylates at 1607 and 1466 cm^{-1}, respectively. Figure 4 shows the structure of the dinuclear monocation in **4**; Table VI gives selected bond distances and angles. The (μ-hydroxo)bis(μ-acetato)dizinc(II) core is capped by two tridentate macrocycles. The zinc ions are each in a distorted octahedral ligand environment. Structures of the analogous Mn^{II},[21] Fe^{II},[22] Co^{II},[23] and Ni^{II}[24] complexes have been prepared previously and are all structurally characterized. The nonbonding intramolecular Zn···Zn distance in **4** is at 3.311 (2) Å. This distance is at 3.35 Å in the Mn^{II}_2, at 3.32 Å in the Fe^{II}_2, at 3.80 Å in the Co^{II}_2, and at 3.40 Å in the Ni^{II}_2 dinuclear complex.

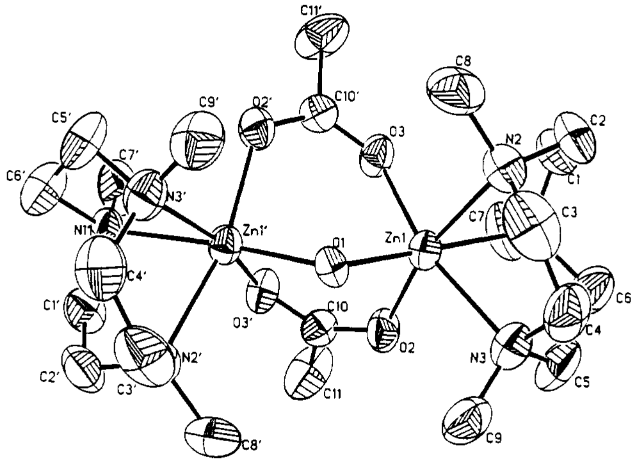

Figure 4. Structure of monocation in crystals of **4**.

Discussion

Structural features of at least two non-heme iron metalloproteins containing a dinuclear active site have in the past years been surprisingly well modeled by low-molecular-weight synthetic analogues.[25,27] Hemerythrin and the iron-containing ribonucleotide reductase, both of which have been characterized by X-ray crystallography at a high enough resolution to definitely show the bridging ligands,[26] are the paradigma for this notion. It is gratifying and of significance that the nonbonding Fe···Fe distances as defined by symmetric carboxylate and oxo bridges in the metalloproteins and in the model compounds usually agree

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within 0.05 Å.[25,27,28] It would therefore appear that the polypeptide chains in such metalloproteins to which the metal ions are coordinated do not greatly influence these distances; they are predominantly defined by the spatial requirements of the bridging ligands.

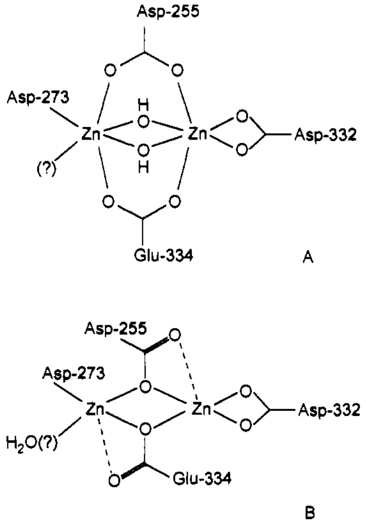
Recently a high-resolution crystal structure of the zinc-containing phospholipase C from *B. cereus* has been reported.[4] A schematic sketch of the dinuclear part of the three zinc ion containing active site is shown in Chart I. Interestingly, these two five-coordinate metal ions are bridged by a symmetric carboxylate (Asp-122) and a hydroxo (or water) bridge—as in the above mentioned ribonucleotide reductase.[26b] The Zn···Zn distance is at 3.3 Å, which is in excellent agreement with Que's iron(III)-containing dinuclear model complex $[Fe_2(TPA)_2(\mu\text{-}O)(\mu\text{-}OBz)](ClO_4)_3\cdot 2H_2O$[28] (Table VII). Furthermore, Krebs et al.[29] have recently synthesized a dinuclear model complex with a six-coordinate and a five-coordinate zinc ion bridged by a symmetric benzoate and a μ-phenoxy bridge. The Zn···Zn distance is at 3.443 Å. This again stresses the point made above that the metal···metal distance in dinuclear active sites is primarily governed by the nature and mode of coordination of the bridging groups. It is also interesting that the metal···metal distances in the zinc-containing enzyme phospholipase C and in the iron-containing ribonucleotide reductase (ferric form) are very similar despite differences in the nature of the metals and oxidation states and the fact that the latter contains a bridging oxo rather than a bridging hydroxo (or water) ligand. Specifically, all metalloproteins and model complexes containing a (μ-oxo(hydroxo))(μ-carboxylato)dimetal or (μ-oxo(hydroxo,aqua))bis(μ-carboxylato)dimetal core have metal-to-metal distances > 3.1 Å.

It is therefore rather surprising and interesting that in the recently published crystal structure of the zinc-containing enzyme leucine aminopeptidase a very short zinc···zinc distance at 2.88 Å has been observed.[5] At 2.7-Å resolution the structure does not yet reveal all details of the first coordination sphere of the zinc atoms but it appears to be clear that two bridging carboxylates (Asp-255 and Glu-334) are present. Lipscomb et al. have stressed the uniqueness of this active site and have at the same time pointed out the possible analogy to the structure of myohemerythrin (Fe···Fe = 3.23 Å),[26a] which contains two symmetric carboxylato bridges and a μ-oxo bridge. Our synthetic model complex **4** contains a (μ-hydroxo)bis(μ-acetato)dizinc(II) core. The zinc-to-zinc distance is at 3.31 Å, which is obviously too large to match the 2.9 Å distance in leucine aminopeptidase well.

We therefore argue that the myohemerythrin core is not a good model for the active site in leucine aminopeptidase. Two *symmetrically* bridging didentate carboxylates with or without additional bridging oxo, hydroxo, or water ligands cannot bring two zinc ions at such a close distance of 2.9 Å as may readily be seen from the compilation of structural data on dinuclear zinc complexes in Table VII.

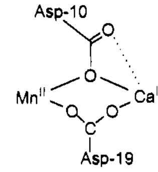
It is well-known in coordination chemistry of dinuclear complexes with two single atom bridging ligands that metal-to-metal distances between ≈2.5 and ≈3.0 Å can be achieved provided that no metal–metal bonding prevails. Edge-sharing polyhedra where the metals may be four-, five-, or six-coordinate with two bridging oxygen atoms (oxide, hydroxide, water) can accommodate two metal ions at this distance. The structures of bis(μ-hydroxo)- and bis(μ-phenoxo)dizinc(II) complexes clearly display this range of Zn···Zn distances (Table VII). Complex **3** with two five-coordinate zinc ions and two μ-hydroxo bridges has a Zn···Zn distance at 3.02 Å.

Chart II. Proposed Structures for the Active Site in Leucine Aminopeptidase (See Text)



Relatively short Zn···Zn distances can also be achieved by four symmetric carboxylate bridges or, alternatively, by two such bridging groups if two additional hydroxo or water ligands are present. The former structure cannot model leucine aminopeptidase because only two bridging carboxylates were detected; there are no other suitable amino acids in the proximity of the zinc atoms. Bridging or terminal hydroxo or aqua ligands have at 2.7-Å resolution also not been detected. Thus, although sketch A in Chart II would be a possible model for the active site, provided that the carboxylates of Asp-255 and Glu-334 are didentate symmetrically bridging and two additional OH or H_2O bridges are present, we do not favor this model.

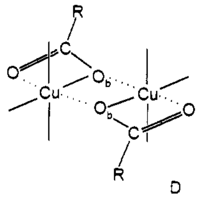
As Lipscomb et al.[5] have already deduced from a difference electron density contour map at 3σ, the carboxylate groups of Asp-255 and Glu-334 are most probably not symmetrically bridging but provide each only one oxygen atom to form two Zn–O–Zn bridges instead. This bridging mode for a monodentate carboxylate is not unprecedented in metalloproteins. In concanavalin A a Mn(II) ion is bridged by aspartate-10 to a calcium ion in this fashion[30] (structure C). The carbonyl oxygen forms an additional, very weak bond to the calcium ion. One other symmetrical didentate carboxylate bridge (Asp-19) is also present which leads to a $Mn^{II}\cdots Ca^{II}$ separation of 4.25 Å.



C

This asymmetric monodentate mode of coordination of a carboxylate has also been identified by X-ray crystallography in dinuclear transition metal complexes.[31]

A number of copper(II) complexes have been structurally characterized which contain two bridging monodentate carboxylates.[32] They all contain the core of structure D. Cu···Cu



D

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distances are observed at ≈3.4 Å. It is noted that the monodentate μ-carboxylate bridges forming a Cu_2O_2 core are asymmetric with a short Cu-O_b and a long Cu···O_b bond. This is due to the fact that the Cu atoms are in a square based pyramidal environment and the bridging carboxylate oxygen atom is coordinated to the basal plane of one Cu center (short Cu–O) and to an apical position (long Cu–O) of the second Cu ion and vice versa. This represents the usual electronically determined configuration of a d^9 Cu(II) center. Zn(II) possesses a d^{10} electron configuration, and as is well documented in complex **3**, the two basal Zn–N distances are slightly *longer* than the corresponding apical distance (Δ(Zn–N) = 0.08 Å). This is in contrast to the isostructural copper complex $[L'_2Cu_2(\mu\text{-OH})_2](ClO_4)_2$, where the basal Cu–N distances are shorter by 0.16 Å than the apical Cu–N bond.

If we now envisage the above bis(μ-carboxylato)dicopper(II) core structure with zinc(II) instead of copper(II), it is quite reasonable to assume that the Zn–O_b distances are equivalent, forming two symmetrical monodentate carboxylate bridges. This would bring the zinc atoms much closer together, and a Zn···Zn distance at ≈3.0 Å is not unreasonable.

In conclusion, we propose that the active site in leucine aminopeptidase may contain the unique structure **B** shown in Chart II. This proposal takes into account all the structural details available at 2.7-Å resolution and the known coordination chemistry of zinc(II). Finally, we suggest that the loosely bound zinc ion has an additional coordinated water molecule which may be activated via hydrogen bonding to the carbonyl oxygen of Asp-273 in a fashion similar to that in complex **2**.

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Registry No. **1**, 139240-64-5; **2**, 139168-41-5; **3**, 139168-43-7; **4**, 139168-46-0; $[L_2Zn](ClO_4)_2$, 139240-65-6; phospholipase C, 9001-86-9; leucine aminopeptidase, 9001-61-0.

Supplementary Material Available: For complexes **1–4**, listings of crystallographic data, calculated positions of hydrogen atoms, bond lengths and angles, and anisotropic thermal parameters (24 pages); tables of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

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Influence of the 5-Substituent of Uracils and Uridines on η^2 Coordination of $Ru^{II}(hedta)^-$ at the C-5–C-6 Bonds

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The coordination of $Ru^{II}(hedta)^-$ with 5-substituted uracils and uridines (X = F, Cl, Br, I, and COOH as 5-substituents) has been studied by ^1H and ^{19}F NMR spectroscopy in combination with electrochemical methods (CV, DPP). Characteristic CV/DPP waves for the η^2-type coordination for $Ru(hedta)^-$, found previously for uridine- and cytidine-related ligands, has been observed in all cases except for X = COOH, which is bound at N-3. $E_{1/2}$ values in the range 0.61–0.79 V vs NHE are recorded for the η^2 isomers; the fluorouracil and fluorouridine complexes have the most positive $Ru^{III/II}$ waves at 0.76 and 0.79 V, respectively. The ^{19}F resonance is shifted upfield upon coordination of $Ru(hedta)^-$ with 5-fluorouracil (5-FU); the η^2-bound isomer is 21.5 ppm upfield of the free ligand; N-3-bound 5-FU exhibits a 26.7 ppm upfield shift. The H-6 position may be shifted either upfield or downfield of the free ligand on coordination. The largest upfield shifts occur for iodo derivatives, ca. 0.88 ppm in 5-iodouridine. The percentage of the η^2-bound isomer is a sensitive function of the Hammett substituent constant, σ_p. η^2 form of $Ru^{II}(hedta)L^-$ occurs at 0% for X = CH_3 and 59% for X = H and reaches a maximum of 85% for X = Cl. The 80% η^2-bound/20% N-3-bound distribution for X = Br shows that the absence of the η^2 form for X = CH_3 (nucleobase T) is not due to steric hinderance but rather due to the σ-electron donation of CH_3 compared to the withdrawing influence of X = F, Cl, Br, and I. The latter three give η^2/N-3 ratios of ca. 5.7. With 5-fluorocytosine the η^2/N-3 ratio is 0.39, favoring N-3 complexes 2.6:1. Cytosines and cytidines were previously observed to favor N-3 modes by 7.3:1.0. Thus, the influence of a 5-fluoro group assists η^2 binding even for a cytosine ring.

Introduction

$Ru^{II}(hedta)^-$, where $hedta^{3-}$ = *N*-(hydroxyethyl)ethylenediaminetriacetato, was recently observed to adopt an η^2-coordination mode at the C-5–C-6 bonds of cytidine (C) and uridine (U).[1] This coordination mode for $Ru^{II}(hedta)^-$ is unique among the other 725 reported metal complexes of pyrimidine nucleobases and nucleosides.[2] The association constants for η^2 binding of pyrimidine nucleobases by ML_n = $Ru^{II}(hedta)^-$ is about 400-fold higher than $Ru^{II}(NH_3)_5^{2+}$ and 90-fold better than $Os(NH_3)_5^{2+}$.[1,3] The η^2 coordination of these three ML_n units occurs competitively with coordination at the N-3 sites of C and U; the N-3 metalation is the normal binding position of pyrimidine nucleobases.[4-11] Somewhat surprisingly, the DNA nucleobase thymidine (T) does not exhibit η^2 coordination at the C-5–C-6 bond with $Ru^{II}(hedta)^-$.[1] At the time of the original discovery of this η^2-coordination mode for C and U, and its absence for T, we speculated that the

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