

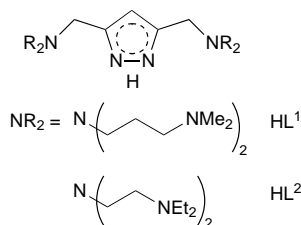
An intramolecular H_3O_2 bridge as the resting form of an active metal-bound hydroxide in a dinuclear zinc(II) complex

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An intramolecular $\text{Zn}-\text{O}_2\text{H}_3-\text{Zn}$ bridge as a complexed form of metal-bound hydroxide exhibits enhanced reactivity compared to the related $\text{Zn}-\text{OH}-\text{Zn}$ unit, illustrated by the reaction with CO_2 .

Various hydrolytic metalloenzymes are known to contain two or more divalent metal ions in close proximity within their active site,¹ and in particular the coordinatively flexible Zn^{II} is found in several native systems like alkaline phosphatase (AP),^{2a} P1 nuclease^{2b} and phospholipase C (PLC).^{2c} Although different and specific mechanisms for the individual catalytic processes are most probably involved, it is believed to be a dominant feature that a metal hydroxide intermediate produced by the deprotonation of zinc-bound water hydrolytically attacks the substrate which itself might be activated by coordination to an adjacent metal ion.¹ Consequently there is considerable interest in the design of polynuclear metal complexes containing $\text{Zn}-\text{OH}_2$ or $\text{Zn}-\text{OH}$ functions to serve as models for these hydrolytic zinc enzymes,^{3,4} however hydrolytically active systems with a di- or tri-nuclear zinc core have still remained rare.⁵ Recently a combination of both $\text{Zn}-\text{OH}_2$ and $\text{Zn}-\text{OH}$ has been reported in the form of an intermolecular $\text{Zn}-\text{O}_2\text{H}_3-\text{Zn}$ bridge and suggested to represent a new structural and possibly functional motif in oligozinc enzyme chemistry.⁶ Here we report the synthesis and structural characterisation of a discrete dinuclear zinc(II) complex incorporating an intramolecular H_3O_2^- bridge as well as evidence for its enhanced reactivity compared to the frequently observed $\text{Zn}-\text{OH}-\text{Zn}$ function.⁴



Ligands L^1 and L^2 are employed, which have been shown to predominantly form dinuclear complexes with five-coordinate N_4X ligation for divalent 3d transition metal ions.⁷⁻⁹ Thereby the range of accessible metal-metal separations can be selectively tuned by altering the chain length of the chelating side arms attached to the pyrazolate heterocycle,⁹ *i.e.* the choice of either L^1 or L^2 . Deprotonation of HL^1 by means of BuLi and subsequent reaction with 2 equiv. of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaBPh_4 affords the dinuclear zinc(II) complex $\mathbf{1}^+$ whose molecular structure has been determined by X-ray diffraction§ (Fig. 1), thereby confirming that a monoatomic oxygen bridge spans two five-coordinate zinc atoms with a metal-metal separation of $d(\text{Zn} \cdots \text{Zn}) = 3.613 \text{ \AA}$. Although its proton could not be located in the crystallographic analysis, a sharp IR absorption at 3618 cm^{-1} clearly identifies this secondary bridge as a discrete metal-bound hydroxide.

In contrast, a similar synthetic procedure starting from HL^2 yields a bimetallic complex $\mathbf{2}$ with an intramolecular H_3O_2^- bridging moiety as revealed by a single crystal X-ray crystallo-

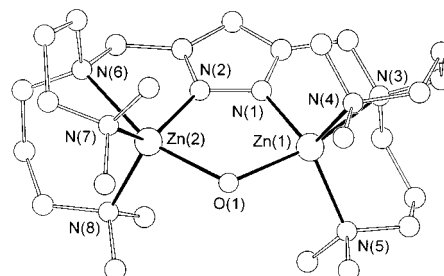


Fig. 1 Molecular structure of the cation of **1**. Selected atomic distances (\AA) and bond angles ($^\circ$): $\text{Zn}(1)-\text{O}(1)$ 2.132(2), $\text{Zn}(1)-\text{N}(1)$ 1.969(3), $\text{Zn}(1)-\text{N}(3)$ 2.480(3), $\text{Zn}(1)-\text{N}(4)$ 2.089(3), $\text{Zn}(1)-\text{N}(5)$ 2.101(3), $\text{Zn}(2)-\text{O}(1)$ 2.149(2), $\text{Zn}(2)-\text{N}(2)$ 1.959(3), $\text{Zn}(2)-\text{N}(6)$ 2.437(3), $\text{Zn}(2)-\text{N}(7)$ 2.099(3), $\text{Zn}(2)-\text{N}(8)$ 2.101(3), $\text{Zn}(1) \cdots \text{Zn}(2)$ 3.613; $\text{O}(1)-\text{Zn}(1)-\text{N}(3)$ 159.2(1), $\text{O}(2)-\text{Zn}(2)-\text{N}(6)$ 160.7(1), $\text{Zn}(1)-\text{O}(1)-\text{Zn}(2)$ 115.1(1).

graphic analysis (Fig. 2). Obviously the shorter side arms of L^2 pull the two metal centres back and apart [$d(\text{Zn} \cdots \text{Zn}) = 4.374 \text{ \AA}$] and thus prevent a bridging position for the small hydroxide ion. Incorporation of an additional water molecule then establishes the H_3O_2^- unit with a very strong intramolecular hydrogen bridge [$d[\text{O}(1) \cdots \text{O}(2)] = 2.462 \text{ \AA}$],¹⁰ where the remaining H atoms are involved in weak hydrogen bonding to two acetone solvent molecules incorporated in the crystal lattice [$d[\text{O}(1) \cdots \text{O}(4)] = 2.875 \text{ \AA}$; $d[\text{O}(1) \cdots \text{O}(5)] = 3.050 \text{ \AA}$]. The H_3O_2^- entity in **2** might be viewed as a hydrated and thereby protected form of a Zn -bound OH^- . For a related $\text{FHO}(\text{H})$ -bridged dicobalt complex⁹ evidence could be obtained for the reversible extrusion of the incorporated water molecule, which in **2** would generate an active $\text{Zn}-\text{OH}$ function in close vicinity

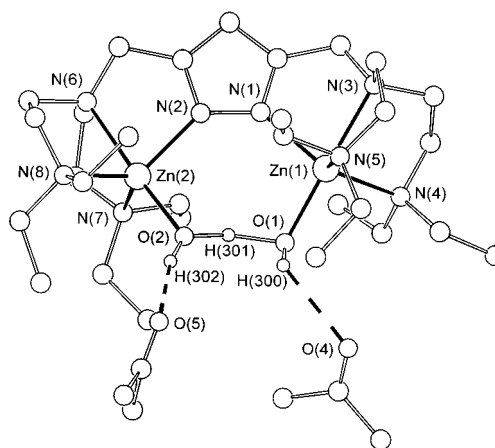


Fig. 2 Molecular structure of the cation of **2**. Selected atomic distances (\AA) and bond angles ($^\circ$): $\text{Zn}(1)-\text{O}(1)$ 1.961(5), $\text{Zn}(1)-\text{N}(1)$ 2.057(6), $\text{Zn}(1)-\text{N}(3)$ 2.231(6), $\text{Zn}(1)-\text{N}(4)$ 2.224(6), $\text{Zn}(1)-\text{N}(5)$ 2.199(6), $\text{Zn}(2)-\text{O}(2)$ 1.969(5), $\text{Zn}(2)-\text{N}(2)$ 2.070(6), $\text{Zn}(2)-\text{N}(6)$ 2.248(6), $\text{Zn}(2)-\text{N}(7)$ 2.208(7), $\text{Zn}(2)-\text{N}(8)$ 2.199(7), $\text{Zn}(1) \cdots \text{Zn}(2)$ 4.374, $\text{O}(1) \cdots \text{O}(2)$ 2.462, $\text{O}(1) \cdots \text{O}(4)$ 2.875, $\text{O}(2) \cdots \text{O}(5)$ 3.050; $\text{O}(1)-\text{Zn}(1)-\text{N}(3)$ 171.1(2), $\text{O}(2)-\text{Zn}(2)-\text{N}(6)$ 174.3(3).

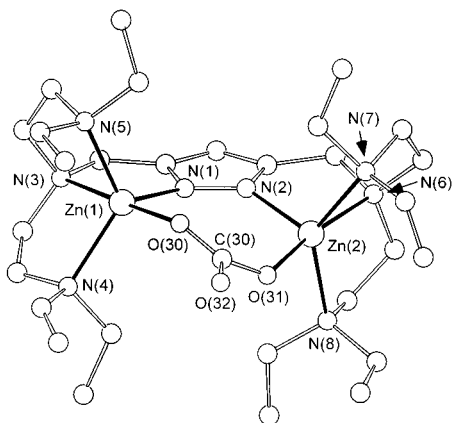


Fig. 3 Molecular structure of the cation of **3**. Selected atomic distances (Å) and bond angles (°): Zn(1)–O(30) 2.009(5), Zn(1)–N(1) 2.028(8), Zn(1)–N(3) 2.255(7), Zn(1)–N(4) 2.155(6), Zn(1)–N(5) 2.113(9), Zn(2)–O(31) 2.027(5), Zn(2)–N(2) 1.987(7), Zn(2)–N(6) 2.253(8), Zn(2)–N(7) 2.153(8), Zn(2)–N(8) 2.185(7), Zn(1)···Zn(2) 4.180; O(30)–Zn(1)–N(3) 177.1(3), O(31)–Zn(2)–N(6) 171.4(3), O(30)–C(31)–O(31) 132.5(8).

to a second Lewis-acidic Zn centre. In order to test the expected higher reactivity of **2** compared to **1**, CO₂ was bubbled into solutions of the complexes in acetone. While no reaction was detected for **1**, the appearance of strong IR bands at 1618 and 1401 cm⁻¹ for **2** indicates the readily occurring absorption of CO₂ with formation of the bicarbonate complex **3**, whose crystal structure is presented in Fig. 3.

In conclusion the reactivity of these dinuclear complexes is drastically varied by appropriate changes of the ligand matrix, *i.e.* of the chelating side arms attached to the pyrazolate. The intramolecular Zn–O₂H₃–Zn bridge as characterised structurally for **2** can be viewed as a hydrated and thus resting form of an active Zn–OH function in close proximity to a second zinc ion capable of binding potential substrate molecules. It thus resembles the oligonuclear array of zinc ions with intermetallic distances larger than 4 Å found in the active sites of metalloenzymes like PLC and P1 nuclease. As evidenced by the reaction with CO₂, **2** exhibits enhanced reactivity compared to the corresponding OH-bridged complex and should thus be a promising candidate for inducing the hydrolytic cleavage of various substrates, which is presently under investigation.

Acknowledgement is made to Professor Dr G. Huttner for his generous and continuous support of our work as well as to the Deutsche Forschungsgemeinschaft (Habilitationstipendium for F. M.) and the Fonds der Chemischen Industrie. We thank Dr F. Rominger and Professor Dr P. Hofmann for collecting the X-ray data of complex **3**.

Notes and References

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‡ Satisfactory elemental analyses were obtained for all new complexes.

§ *Crystal data*: for **1**: C₇₃H₉₄B₂N₈OZn₂, *M* = 1252.0, triclinic, space group *P* $\bar{1}$, *a* = 11.793(2), *b* = 14.705(3), *c* = 20.064(4) Å, α = 100.29(2), β = 99.64(1), γ = 101.06°, *U* = 3286(1) Å³, *Z* = 2, *D_c* = 1.264 g cm⁻³, μ (Mo–K α) = 0.780 mm⁻¹, 8905 reflections observed [*I* > 2 σ (*I*)], 828 parameters, largest difference peak 1.010 e Å⁻³, final *R*, *R_w* on [*I* > 2 σ (*I*)] data were 0.049, 0.1140, goodness of fit on *F*² = 1.111. For **2**: C₇₇H₁₀₄B₂N₈O₂Zn₂·2.5C₃H₆O, *M* = 1471.3, monoclinic, space group *P*₂/c, *a* = 17.974(5), *b* = 26.809(6), *c* = 17.543(4) Å, β = 92.11(1)°, *U* = 8448(4) Å³, *Z* = 4, *D_c* = 1.183 g cm⁻³, μ (Mo–K α) = 0.621 mm⁻¹, 6527 reflections observed [*I* > 2 σ (*I*)], 831 parameters, largest difference peak 1.008 e Å⁻³, final *R*, *R_w* on [*I* > 2 σ (*I*)] data were 0.078, 0.1816, goodness of fit on *F*² = 1.036. For **3**: C₇₈H₁₀₂B₂N₈O₃Zn₂·C₃H₆O, *M* = 1410.2, monoclinic, space group *P*₂/c, *a* = 17.5944(2), *b* = 12.9761(2), *c* = 48.2254(1) Å, β = 90.530(1)°, *U* = 7880.1(2) Å³, *Z* = 4, *D_c* = 1.188 g cm⁻³, μ (Mo–K α) = 0.661 mm⁻¹, 8889 reflections observed [*I* > 2 σ (*I*)], 801 parameters, largest difference peak 1.501 e Å⁻³, final *R*, *R_w* on [*I* > 2 σ (*I*)] data were 0.115, 0.322, goodness of fit on *F*² = 1.061. All structures were solved by direct methods with the SHELXS-97 and refined with the SHELXL-97 programs.¹¹ CCDC 182/815.

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Received in Basel, Switzerland, 15th January 1998; 8/004121