A Dinuclear Zinc(II) Complex of 2,6-bis{[(2-hydroxybenzyl)(2-pyridylmethyl)amino]methyl}-4-methylphenol Bearing an Exogenous Hydroxo Bridge

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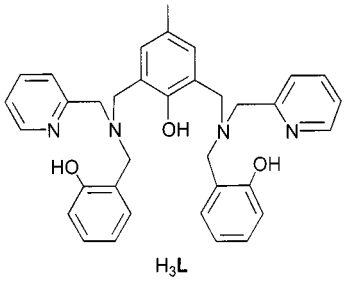
Reaction of the symmetrical proligand H_3L with zinc(II) perchlorate gives a product from which the cationic complex $[Zn_2L(OH_2)_3]ClO_4$ and the neutral complex $[Zn_2L(OH)]$ co-crystallise in the triclinic space group $P\bar{1}$, with unit cell parameters a = 14.7647(13), b = 16.9376(14), c = 17.8089(15) Å, α = 68.634(2)°, β = 71.356(2)°, γ = 87.526(2)°. The dinuclear zinc centre in $[Zn_2L(OH_2)_3]^+$ is endogenously bridged by a cresolato-O atom; in $[Zn_2L(OH)]$ this bridging mode is enhanced by an exogenous hydroxo bridge.

Introduction

The symmetric "end-off" compartmental proligand 2,6-bis{[(2-hydroxybenzyl)(2-pyridylmethyl)amino]methyl}-4-methylphenol (H_3L) has been used to generate homodinuclear donor asymmetric nickel(II) ethanoato- and coordination number asymmetric zinc(II) ethanoato complexes.[1] The crystal structures revealed the presence of a (μ-cresolato)(μ-ethanoato)-bridged dinuclear core in each complex with the (μ-cresolato) bridge endogenous and the (μ-ethanoato) bridge exogenous in nature. Noncoordinated ethanoic acid molecules were tightly hydrogen-bonded to the pendant phenols of the ligand generating a double acid salt of the type $[CH_3COO\cdots H\cdots L\cdots H\cdots OOCCH_3]^{3-}$ in the dinickel complex and a single acid salt of the type $[CH_3COO\cdots H\cdots L]^{3-}$ in the dizinc complex. In both cases the ligand periphery has been extended to provide a supraligand in which the donor potential of the original ligand has been enhanced.

The presence of a noncoordinating anion, rather than ethanoate, should inhibit the formation of an anion-based exogenous bridge and encourage interaction of the dinuclear core with the solvent. The reaction of H_3L with zinc perchlorate was therefore investigated and herein we report the effect of a noncoordinating anion on product formation together with the crystal structure of the product.



H_3L

Results and Discussion

H_3L was synthesized by modification of the method of Krebs et al.[2] and reacted with zinc(II) perchlorate in acetonitrile. Colourless crystals, suitable for X-ray structural determination, were obtained on standing. The crystal structure revealed that the cationic complex $[Zn_2L(OH_2)_3]ClO_4$ (**1**) and the neutral complex $[Zn_2L(OH)]$ (**2**) had co-crystallised. The molecular structures of the complexes are shown in Figures 1 and 2 with selected bond lengths and angles given in the captions to the figures. In addition to the complexes two disordered water molecules and a disordered acetonitrile molecule were present in the asymmetric unit.

The structure of complex **1** shows that the complex is coordination number asymmetric[3] with one zinc atom [Zn(1)] six-coordinate and the second [Zn(2)] five-coordinate. There is an endogenous cresolato bridge at the dinuclear centre but no exogenous bridge. Zn(1) is in a slightly distorted octahedral geometry with an N_2O_4 donor set derived from two ligand cresolato-O and pendant phenolato-O donor atoms [O(1) and O(2)], an articular tertiary aminic-N atom [N(1)], the pyridinyl-N atom [N(2)] and two *cis*-coordinated water molecules [O(4) and O(5)]. One water molecule is *trans* to the cresolato bridge and the other is *trans* to the articular tertiary amine as found at the six-coordinated metal atoms in the structure of the related dinickel(II) complex $[Ni_2L_A(OH_2)_4]\cdot CH_3COO^-\cdot C_3H_7NO\cdot 0.75H_2O$.[4] The three *trans*-axial angles at Zn(1) are 171.8

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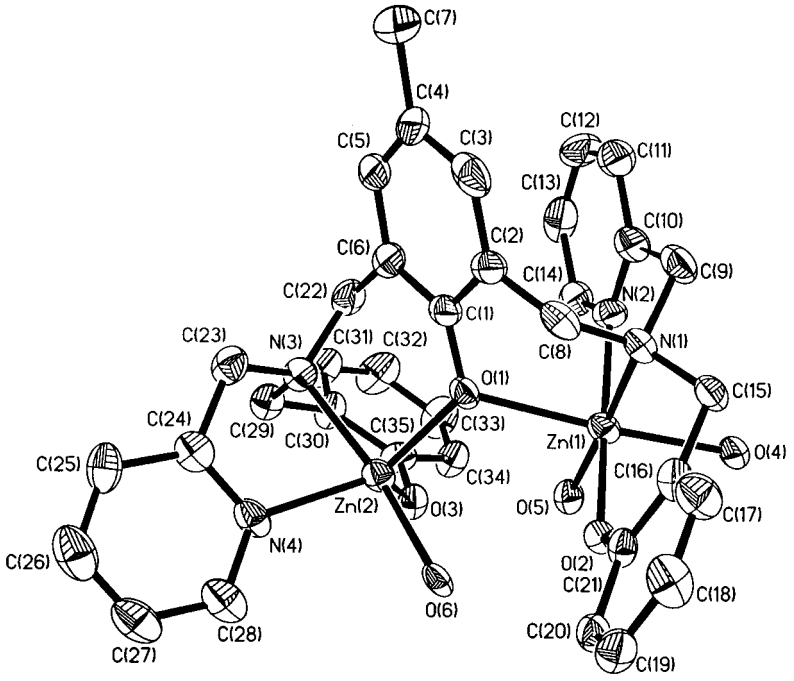


Figure 1. An ORTEP drawing of the molecular structure of the complex cation from (**1**), $[Zn_2L(OH_2)_3]^+$, showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level; selected bond lengths (Å) and angles (°) at the zinc(II) atom: Zn(1)−O(1) 2.241(5), Zn(1)−O(2) 2.023(4), Zn(1)−N(1) 2.166(6), Zn(1)−N(2) 2.100(6), Zn(1)−O(4) 2.164(5), Zn(1)−O(5) 2.036(5), Zn(2)−O(1) 2.009(5), Zn(2)−O(3) 1.952(5), Zn(2)−O(6) 2.065(4), Zn(2)−N(3) 2.153(6), Zn(2)−N(4) 2.131(6), Zn(1)−Zn(2) 3.6162(12); O(2)−Zn(1)−N(2) 171.8(2), O(5)−Zn(1)−N(1) 177.9(2), O(1)−Zn(1)−O(4) 172.51(18), N(2)−Zn(1)−N(1) 82.1(2), N(1)−Zn(1)−O(2) 89.8(2), O(2)−Zn(1)−O(5) 91.26(19), O(5)−Zn(1)−N(2) 96.8(2), N(3)−Zn(2)−O(6) 167.9(2), O(1)−Zn(2)−O(3) 109.4(2), O(3)−Zn(2)−N(4) 117.7(2), N(4)−Zn(2)−O(1) 132.1(2), Zn(1)−O(1)−Zn(2) 116.5(2)

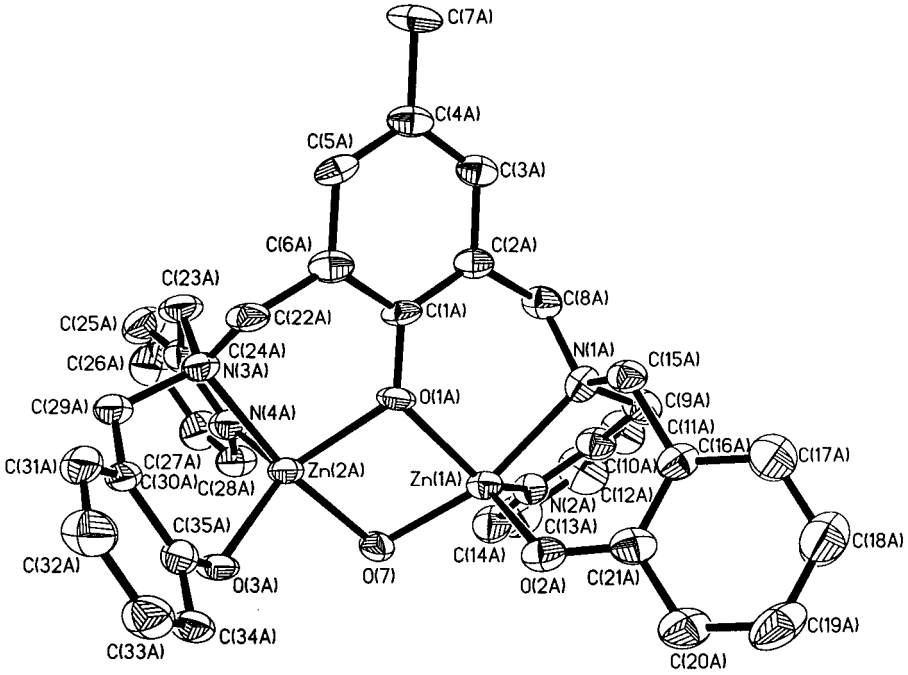
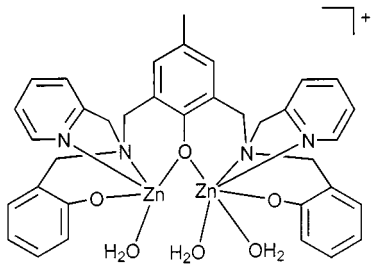
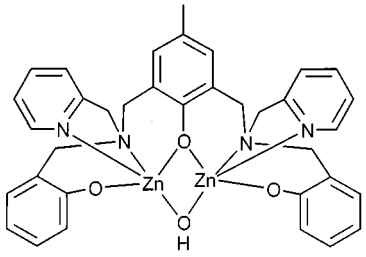


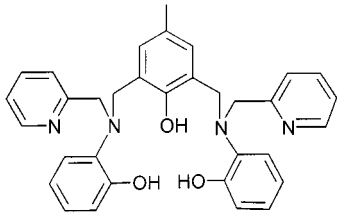
Figure 2. An ORTEP drawing of the molecular structure of $[Zn_2LOH]$ (**2**) showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level; selected bond lengths (Å) and angles (°) at the zinc(II) atom: Zn(1A)−O(1A) 2.048(5), Zn(1A)−O(2A) 1.967(5), Zn(1A)−O(7) 1.990(5), Zn(1A)−N(1A) 2.179(6), Zn(1A)−N(2A) 2.107(6), Zn(2A)−O(1A) 2.066(5), Zn(2A)−O(3A) 1.989(5), Zn(2A)−O(7) 1.975(5), Zn(2A)−N(3A) 2.209(6), Zn(2A)−N(4A) 2.060(7), Zn(1A)−Zn(2A) 3.0696(13); O(7)−Zn(1A)−N(1A) 159.6(2), N(2A)−Zn(1A)−O(1A) 128.2(2), O(1A)−Zn(1A)−O(2A) 109.4(2), O(2A)−Zn(1A)−N(2A) 121.0(2), O(7)−Zn(2A)−N(3A) 169.3(2), O(1A)−Zn(2A)−O(3A) 130.4(2), O(3A)−Zn(2A)−N(4A) 115.8(2), N(4A)−Zn(2A)−O(1A) 112.8(2), Zn(1A)−O(1)−Zn(2A) 96.54(19), Zn(1A)−O(7)−Zn(2A) 101.5(2)



$[Zn_2L(OH_2)_3]^+$



$[Zn_2L(OH)]$



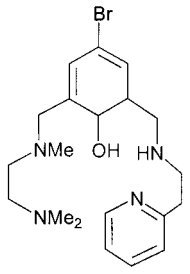
H_3L_A

[O(2)−Zn(1)−N(2)], 177.9 [O(5)−Zn(1)−N(1)] and 172.5° [O(4)−Zn(1)−O(1)].

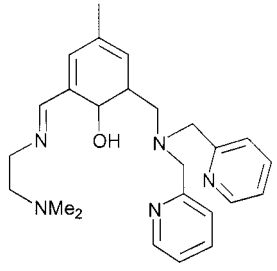
The second zinc atom, Zn(2), is five-coordinate with an N_2O_3 donor set derived from the bridging cresolato-O and pendant phenolato-O donor atoms [O(1) and O(3)], an articular tertiary aminic-N atom [N(3)], the pendant pyridinyl-N atom [(N4)] and one coordinated water molecule [O(6)]. The degree of trigonality (τ) at Zn(2) is 0.60 signifying a distortion towards a trigonal bipyramidal geometry [a perfect trigonal bipyramidal geometry has τ = 1 and a perfect square pyramidal geometry has τ = 0.5].[5] The largest angle at Zn(2) is O(6)−Zn(2)−N(3) (167.9°) indicating that the water molecule and the articular aminic-N atom occupy the axial positions.

The second complex in the asymmetric unit, $[Zn_2L(OH)]$ (**2**), is a neutral dinuclear species with a (μ-cresolato)(μ-hydroxo) core. Both zinc atoms are five-coordinate with N_2O_3 donor sets made up of a bridging cresolato-O atom, a pendant phenolato-O atom, a pyridinyl-N atom, an articular tertiary aminic-N atom and a bridging hydroxo-O atom. The τ values of 0.52 [Zn(1A)] and 0.65 [Zn(2A)] show that the geometries at the metals are intermediate between trigonal bipyramidal and square pyramidal geometry. The largest angles at the metals are 159.6° [O(7)−Zn(1A)−N(1A)] and 169.3° [O(7)−Zn(2A)−N(3A)] showing that the O atom of the exogenous hydroxo bridge is *trans* to the articular tertiary aminic-N atom in each case.

The absence of an exogenous bridge in the complex cation from **1** promotes an intermetallic separation, Zn(1)−Zn(2), of 3.62 Å which is longer than that generally found in complexes bearing a (μ-cresolato)(μ-ethanoato)-bridged dinuclear core (≈3.41 Å)[1,6] and this is mirrored by the open Zn(1)−O(1)−Zn(2) angle of 116.5°. The separation Zn(1A)−Zn(2A) in complex **2** is 3.07 Å which is considerably shorter than those found in complexes with exogenously bridged bidentate bridges.[7] This is accompanied by a narrowing of the cresolato bridging angle [Zn(1A)−O(1A)−Zn(2A): 96.5°] *cf.* 116.5° in complex **1**. The Zn−OH−Zn bridge is slightly asymmetric with Zn−O distances of 1.975(5) and 1.990(5) Å. The bond lengths and angles at the dinuclear centre in complex **2** are similar to those found in the structure of $[Zn_2L_BOH(NO_3)_2]$ derived from the unsymmetrical compartmental ligand HL_B and used in the functional mimicking of metallo-β-lactams.[6] In this molecule the bridging bond angles at the phenolate- and hydroxo-O atoms are 98.2° and 105.7° respectively and the inter-zinc separation is 3.11 Å.



HL_B



HL_C

In the crystal structures of dizinc(II)-containing metalloenzymes a water molecule or hydroxide anion shared by the zinc atoms frequently gives rise to a μ-hydroxo(*aqua*)-dizinc(II) motif[8,9] and the following metalloenzymes serve as representative examples: the metallo-β-lactamases from *Bacteriodes fragilis*[10,11] and *Stenotrophonomonas maltophilia*,[12] phospholipase C from *Bacillus cereus*,[13] P1 nuclease from *Penicillium citrium*[14] and bovine lens leucine aminopeptidase.[15,16] The first two examples have an unsupported water bridge and the Zn···Zn separation is approx. 3.5 Å, the next two examples are doubly bridged, by a water molecule and a bidentate carboxylato group, closing the Zn···Zn separation to approx. 3.3 Å. In the final example there is a triple bridge arising from a water molecule, a monodentate aspartate residue and a bidentate glutamate residue leading to a Zn···Zn separation of approx. 3.0 Å. Complex **2** has a double bridge constituted from two single oxygen atoms [(μ-cresolato)(μ-hydroxo)] and a Zn···Zn separation of 3.07 Å, and is thus similar to that found in bovine lens leucine aminopeptidase.

It is intriguing that the two complexes **1** and **2** co-crystallise and it is possible that conversion of **1** to **2** can occur if one of the polarisable water molecules on one Zn atom[17]

attacks the second Zn atom to displace bound water, thus forming the exogenous hydroxo bridge. Such an opportunity might also arise in the formation of μ-hydroxo bridges in dizinc(II)-containing metalloenzymes. A comparable co-crystallisation has been reported for the related complex $[Zn_2L_C(NCS)_3]$, derived from the phenol-based Schiff base compartmental ligand HL_C, in which one molecule has an exogenously bridging thiocyanate and two terminal thiocyanates, whereas the second molecule has no exogenous bridge and all three thiocyanates are terminal.[18]

Experimental Section

The Bulk Sample of $[ZnL]ClO_4 \cdot 3H_2O$: The proligand H_3L (133 mg, 0.24 mmol) was dissolved in warm CH_3CN (20cm^3) and $Zn(ClO_4)_2 \cdot 6H_2O$ (177 mg, 0. 48 mmol) added. The solution was refluxed gently for 1 h and then cooled to room temperature. Colourless crystals, suitable for X-ray structural analysis, were recovered on standing for one week. Yield: 154 mg (90%). MS (ES): *m*/*z* (%) = 687 (100) $[Zn_2L]^+$. IR (KBr disc): $\tilde{\nu}$ = 1609 cm^{-1} (C=N-pyr), 1572 (C=C-Ar), 1081 (ClO_4). $C_{35}H_{39}ClN_4O_{10}Zn_2$ (841.9): calcd. C 49.6, H 4.7, N 6.9, Cl 4.1; found C 49.9, H 4.7, N 6.7, Cl 4.1.

Caution! Although we have experienced no difficulties with the perchlorate salts they should nevertheless be regarded as hazardous and treated with care.

Crystal Data: $C_{72}H_{80}ClN_9O_{16}Zn_4$: M = 1624.38. Crystallises from CH_3CN as colourless blocks; crystal dimensions 0.28 × 0.15 × 0.06 mm^3. Triclinic, space group $P\bar{1}$, a = 14.7647(13), b = 16.9376(14), c = 17.8089(15) Å, α = 68.634(2)°, β = 71.356(2)°, γ = 87.526(2)°, U = 3916.3(6) Å^3, Z = 2, D_c = 1.377 Mg/m^3, Mo-K_α radiation (λ = 0.71073 Å), μ(Mo-K_α) = 1.312 mm^{-1}, F(000) = 1680. Data collected were measured on a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system at 150 K. Cell parameters were refined from the setting angles of 54 reflections (1.46 < θ < 28.32°). Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 24262 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.7102 and 0.9254), 8804 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed geometrically, except those on O1W, and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R_1 = 0.0822 ($wR2$ = 0.2186, for all 17770 data, 913 parameters, mean and maximum δ/σ 0.004, 0.175) with allowance for the thermal anisotropy of all non-hydrogen atoms. The $[ClO_4]^-$ anion was disordered and refined to an occupancy of 41.0:59.0%; two disordered water molecules [O(2W) and O(3W)] were refined to occupancies of 52.0:48.0 and 51.0:49.0% respectively, and a disordered CH_3CN molecule was refined to an occupancy of 54.0:46.0%. Minimum and maximum final electron density: −1.176 and 2.371 e·Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_0^2) + (0.1212P)^2 + 0.00P]$ where $P = (F_0^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL as implemented on a Viglen Pentium computer.[19]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-171737. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] H. Adams, D. Bradshaw, D. E. Fenton, *Supramolecular Chem.* **2001**, *13*, 513−519.
[2] B. Krebs, K. Schepers, B. Bremer, G. Henkel, E. Althaus, W. Müller-Warmuth, K. Griesar, W. Haase, *Inorg Chem.* **1994**, *33*, 1907−1914.
[3] J. H. Satcher, Jr., M. W. Droege, T. J. R. Weakley, R. T. Taylor, *Inorg. Chem.* **1995**, *34*, 3317−3328.
[4] M. A. de Brito, A. J. Bortoluzzi, A. Greatti, A. S. Ceccato, A. C. Joussef, S. M. Drechsel, *Acta Crystallogr., Sect. C* **2000**, *56*, 1188−1190.
[5] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
[6] N. V. Kaminskaia, B. Spingler, S. J. Lippard, *J. Am. Chem. Soc.* **2000**, *122*, 6411−6422.
[7] D. Bradshaw, PhD Thesis (University of Sheffield), **2001**.
[8] W. N. Lipscomb, N. Sträter, *Chem. Rev.* **1996**, *96*, 2375−2433.
[9] D. E. Wilcox, *Chem. Rev.* **1996**, *96*, 2435−2458.
[10] N. O. Concha, B. A. Rasmussen, K. Bush, O. Herzberg, *Structure* **1996**, *4*, 823−836.
[11] A. Carfi, E. Duée, R. Paul-Soto, N. Galleni, J.-M. Frére, O. Dideberg, *Acta Crystallogr., Sect. D* **1998**, *54*, 47−57.
[12] J. H. Ulla, T. R. Walsh, I. A. Taylor, D. C. Emery, C. S. Verma, S. J. Gamblin, J. Spencer, *J. Mol. Biol.* **1998**, *284*, 125−136.
[13] E. Hough, L. K. Hansen, B. Birknes, K. Jynge, S. Hansen, A. Hordvik, C. Little, E. J. Dodson, Z. Derewenda, *Nature(London)* **1989**, *338*, 357−360.
[14] A. Volbeda, A. Lahm, F. Sakijama, D. Suck, *EMBO J.* **1991**, *10*, 1607−1618.
[15] N. Strater, W. N. Lipscomb, *Biochemistry* **1995**, *34*, 14792−14800.
[16] Further examples of the μ-hydroxo(*aqua*)dizinc(II) motif may be found in the structures of phosphotriesterase from *Pseudomonas diminuta*[20] and dihydroorotase from *Escherichia coli*.[21] In both structures the dinuclear centre is doubly bridged, by a water molecule and a bidentate carbamate group from a carboxylated lysine residue.
[17] B. L. Vallee, D. S. Auld, *Proc. Natl. Acad. Sci. USA.* **1990**, *87*, 220−224.
[18] K. Abe, J. Izumi, M. Ohba, T. Yokoyama, H. Okawa, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 85−95.
[19] SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS Ltd., Madison., Wis., USA, **1997**.
[20] M. M. Benning, H. Shim, F. M. Raushel, H. M. Holden, *Biochemistry* **2001**, *40*, 2712−2722.
[21] J. B. Thoden, G. N. Phillips, Jr., T. M. Neal, F. M. Raushel, H. M. Holden, *Biochemistry* **2001**, *40*, 6989−6997.

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