

Supporting information for

Effect of Metals in Biomimetic Dimetal Complexes on Affinity and Gas-phase Protection of Phosphate Esters

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Synthesis and characterization of dimetallic complexes

Figure S1. A) $[\text{LGa}_2(\text{PO}_4)]^{2+}$, m/z 403 isolated for 30 ms in trap, no collision energy. B) $[\text{LGa}_2(\text{PO}_4)]^{2+}$, m/z 403 isolated for 200 ms in trap, no collision energy.

Figure S2. ITC binding isotherm for titration of 0.11 mM $[\text{LFeZn}(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2$ with 2.47 mM Na_2HPO_4 in 10 mM HEPES.

Figure S3. ITC binding isotherm for titration of 0.20 mM $[\text{LGaCu}(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2$ with 2.47 mM Na_2HPO_4 in 10 mM HEPES.

Figure S4. Energy minimized structures and Cartesian coordinates for $[\text{LGa}_2(\text{PO}_4)]^{2+}$ **[1]**, $[\text{LGa}_2(\text{PO}_4\text{H})]^{3+}$ **[1]H⁺**, $[\text{LGaZn}(\text{PO}_4)]^+$ **[2]**, $[\text{LGaZn}(\text{PO}_4\text{H})]^{3+}$ **[2]H⁺**, $[\text{LZn}_2(\text{PO}_4)]$ **[3]**, and $[\text{LZn}_2(\text{PO}_4\text{H})]^+$ **[3]H⁺**, 2,4-dimethyl-4,5-dihydrooxazole **[4]**, 2,4-dimethyl-4,5-dihydrooxazol-3-ium **[4]H⁺**

Synthesis and characterization of dimetallic complexes

[LInCu(CH₃CO₂)₂](ClO₄)₂. HL (48 mg, 0.084 mmol) dissolved in 1 ml MeOH was mixed with In(ClO₄)₃·6H₂O (43.7 mg, 0.084 mmol) and Cu(ClO₄)₂·6H₂O (31.1 mg, 0.084 mmol) dissolved in 2 ml H₂O. The initially brown solution turned dark green. The solution was placed in a closed vessel with ethyl acetate for vapor diffusion overnight. The dark green crystalline product was isolated by suction filtration and washed twice with cold water and diethyl ether and allowed to dry in air. Yield [LInCu(CH₃CO₂)₂](ClO₄)₂: 46 mg, 51%. CHN calc.: C: 45.02%; H: 4.25%; N: 7.88%. Found: C: 44.43%; H: 4.18%; N: 7.68%. ESI-MS (H₂O:MeCN): 66% [LInCu(O)]²⁺ *m/z* 382.5758 (7.5 ppm), 90% [LInCu(OH)(OH)]²⁺ *m/z* 391.5812 (7.7 ppm), 100% [LInCu(OH)(Cl)]²⁺ *m/z* 400.5641 (7.2 ppm), 64% [LInCu(OH)(CH₃CO₂)]²⁺ *m/z* 412.5835 (7.0 ppm), 64% [LInCu(CH₃CO₂)₂]²⁺ *m/z* 433.5918 (7.1 ppm). IR: $\nu_a(\text{COO})$ 1566 cm⁻¹, $\nu_s(\text{COO})$ 1445 cm⁻¹.

[LGaM(CH₃CO₂)₂](ClO₄)₂ (M = Zn²⁺ or Cu²⁺). HL (50 mg, 0.0874 mmol) dissolved in 3 ml MeOH was mixed with Ga(ClO₄)₃·6H₂O (21 mg, 0.044 mmol) and 1 eq. of M(ClO₄)₂ dissolved in 1 ml H₂O. After 5 min of stirring, the solution was placed in ethyl acetate for vapor diffusion. A light green (Cu²⁺) or white (Zn²⁺) crystalline product formed after 1-2 days. [LGaZn(CH₃CO₂)₂](ClO₄)₂·2H₂O: 25.3 mg, 27.6%. CHN calc.: C: 45.42%; H: 4.67%; N: 8.11%. Found: C: 45.10%; H: 4.28%; N: 8.11%. ESI-MS (MeCN): 100% [LGaZn(CH₃CO₂)₂]²⁺ *m/z* 411.0994 (1.0 ppm). IR: $\nu_a(\text{COO})$ 1577 cm⁻¹, $\nu_s(\text{COO})$ 1434 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂SO) δ = 8.89 (d, J = 4 Hz, 1H), 8.62 (d, J = 4 Hz, 1H), 8.44 (d, J = 8 Hz, 1H), 8.31 (t, J = 8 Hz, 1H), 8.23 (d, J = 4 Hz, 1H), 8.14 (t, J = 8 Hz, 1H), 7.95 (d, J = 8 Hz, 1H), 7.78-7.73 (m, 3H), 7.64 (t, J = 4 Hz, 1H), 7.51-7.46 (m, 2H), 7.20 (t, J = 8 Hz, 1H), 6.85-6.80 (m, 3H), 6.61 (d, J = 8 Hz, 1H), 4.78 (d, J = 16 Hz, 1H), 4.55 (d, J = 12 Hz, 1H), 4.45 (d, 16 Hz, 1H), 4.25 (d, J = 16 Hz, 1H), 4.08 (d, J = 16 Hz, 1H), 3.98 (d, 12 Hz, 1H), 3.87-3.74 (m, 4H), 3.51 (t, J = 16 Hz, 2H), 2.23 (s, CH₃CO₂), 2.18 (s, CH₃CO₂), 1.12 (s, 9H) ppm. [LGaCu(CH₃CO₂)₂](ClO₄)₂: 46.1 mg, 51%. CHN calc.: C: 47.01%; H: 4.44%; N: 8.22%. Found: C: 46.26%; H: 4.30%; N: 8.08%. ESI-MS (MeCN): 100% [LGaCu(CH₃CO₂)₂]²⁺ *m/z* 410.6020 (5.4 ppm). IR: $\nu_a(\text{COO})$ 1566 cm⁻¹, $\nu_s(\text{COO})$ 1445 cm⁻¹.

Methylated β cas phosphopeptide. β cas phosphopeptide (10 μ l, 4.9 nmol) was dried to completion in a SpeedVac for 6 h. Thionyl chloride (40 μ l, 0.55 nmol) was added dropwise (Caution! Thionyl chloride reacts violently with trace amounts of water) to 500 μ l anhydrous methanol. The freshly prepared methanolic hydrochloride was added to the dried peptide and the solution was sonicated for 15 min. After reaction for 2 h at RT, the peptide was dried to completion in a SpeedVac and reconstituted in H₂O:MeCN 3:1 before use. ESI-MS revealed several ions that were assigned to different stages of methylation, including the desired complete (7x CH₂, +98 Da) methylated peptide at [M+2H]²⁺ *m/z* 1080.4717 (<1 ppm), [M+3H]³⁺ *m/z* 720.6503 (<1 ppm).

Dephosphorylated β cas phosphopeptide. β cas phosphopeptide (10 μ l, 4.9 nmol) was dried in a SpeedVac and dissolved in 20 μ l, 50 mM tetraethylammonium bicarbonate (TEAB), pH 8. Alkaline phosphatase (2 μ l) was added and the solution was incubated at 37°C for 2 h. The solution was acidified with 1 μ l 10% trifluoroacetic acid (TFA) and purified on a R3 microcolumn (eluent: 50% MeCN, 0.1% formic acid). The eluted peptide was dried on a SpeedVac. Complete dephosphorylation was confirmed by ESI-MS, [M+2H]²⁺ *m/z* 991.4401 (5.4 ppm).

Comment to Figure S1. The m/z 411.0685 ions can also be formulated as the isobaric ion $[\text{LGa}_2(\text{HPO}_4)(\text{HO})]^{2+}$. However, isolation without collision activation of $[\text{LGa}_2(\text{PO}_4)]^{2+}$ for 30 ms and 200 ms revealed that the ion at m/z 411.0685 was due to the reaction of the phosphate loss ion, $[\text{LGa}_2(\text{PO}_4)]^{2+}$ with residual water vapor in the linear ion-trap of the mass spectrometer.

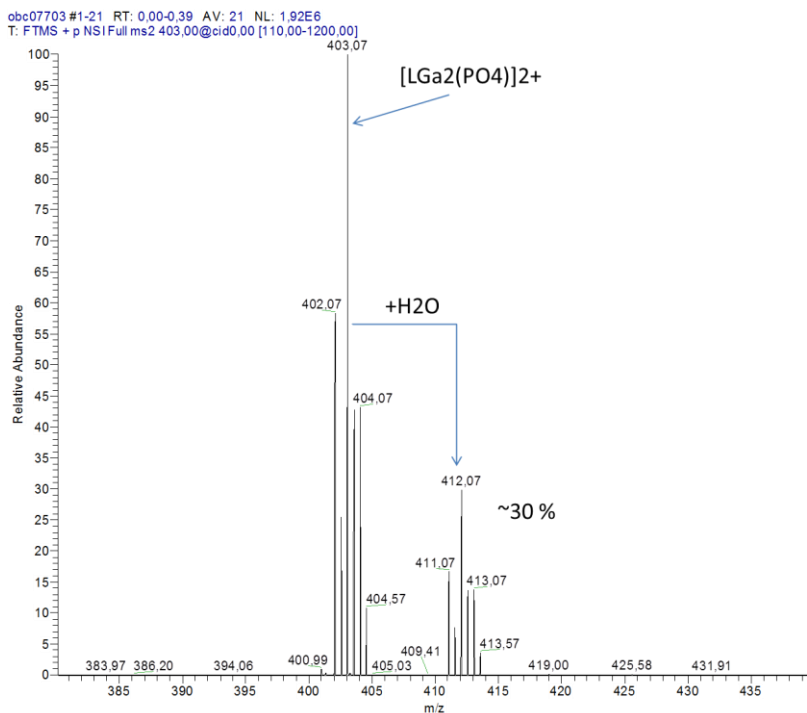


Figure S1A. $[\text{LGa}_2(\text{PO}_4)]^{2+}$, m/z 403.07 isolated for 30 ms in trap, no collision energy.

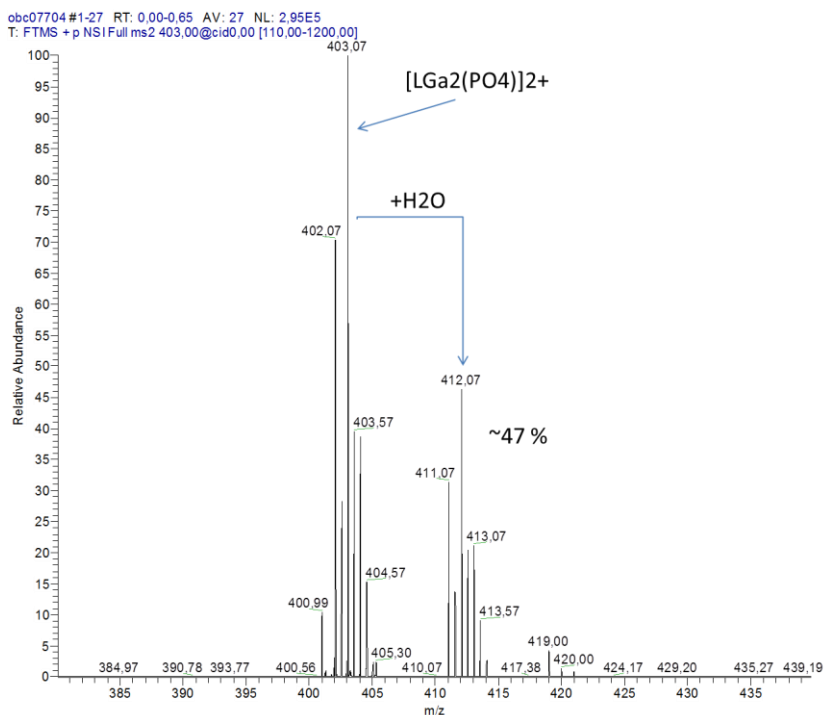


Figure S1B. $[\text{LGa}_2(\text{PO}_4)]^{2+}$, m/z 403.07 isolated for 200 ms in trap, no collision energy.

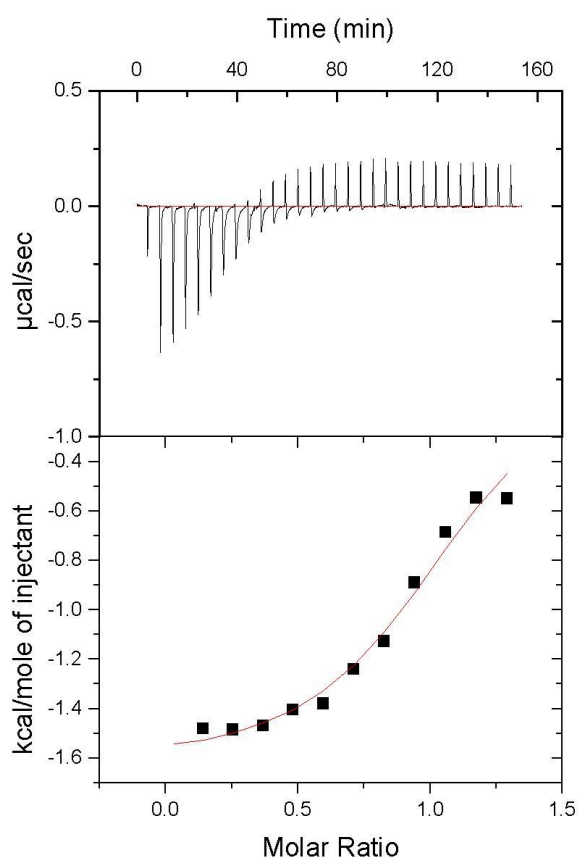


Figure S2. ITC binding isotherm for titration of 0.11 mM $[\text{LFeZn}(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2$ with 2.47 mM Na_2HPO_4 in 10 mM HEPES.

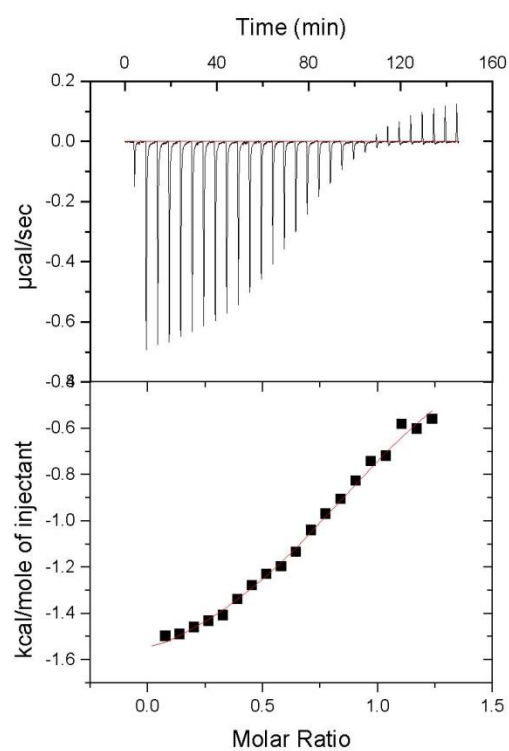
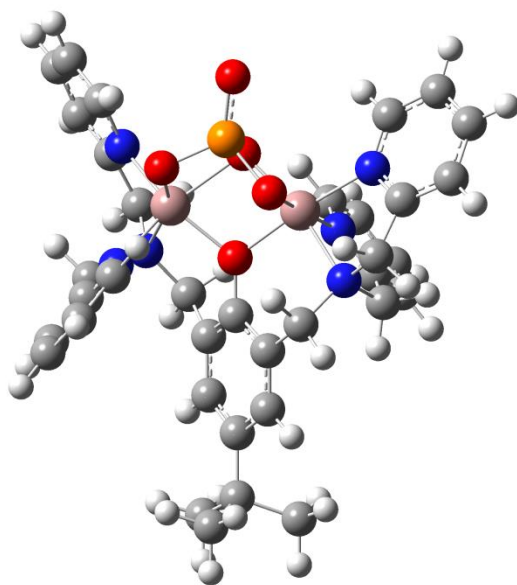


Figure S3. ITC binding isotherm for titration of 0.20 mM $[\text{LGaCu}(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2$ with 2.47 mM Na_2HPO_4 in 10 mM HEPES.

Figure S4: Energy minimized structures and Cartesian coordinates for $[\text{LGa}_2(\text{PO}_4)]^{2+}$ **[1]**, $[\text{LGa}_2(\text{PO}_4\text{H})]^{3+}$ **[1]H⁺**, $[\text{LGaZn}(\text{PO}_4)]^+$ **[2]**, $[\text{LGaZn}(\text{PO}_4\text{H})]^{3+}$ **[2]H⁺**, $[\text{LZn}_2(\text{PO}_4)]$ **[3]**, and $[\text{LZn}_2(\text{PO}_4\text{H})]^+$ **[3]H⁺**, 2,4-dimethyl-4,5-dihydrooxazole **[4]**, 2,4-dimethyl-4,5-dihydrooxazol-3-ium **[4]H⁺**

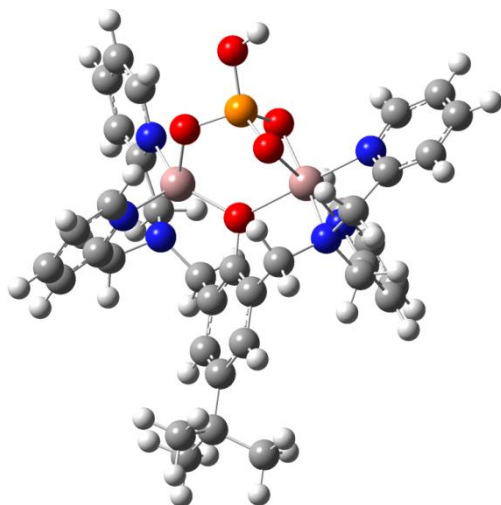
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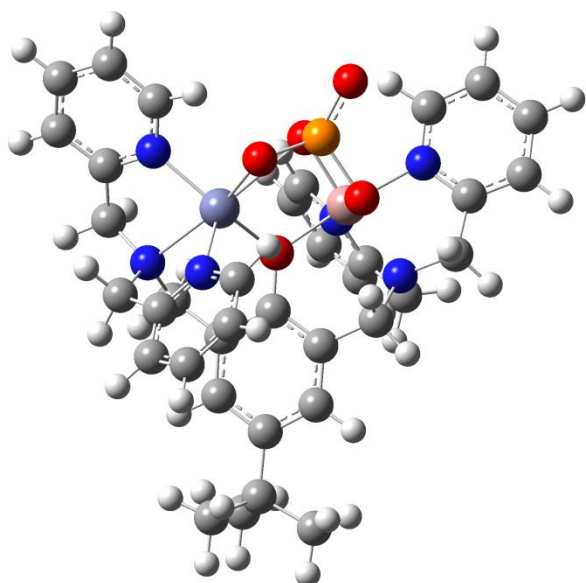
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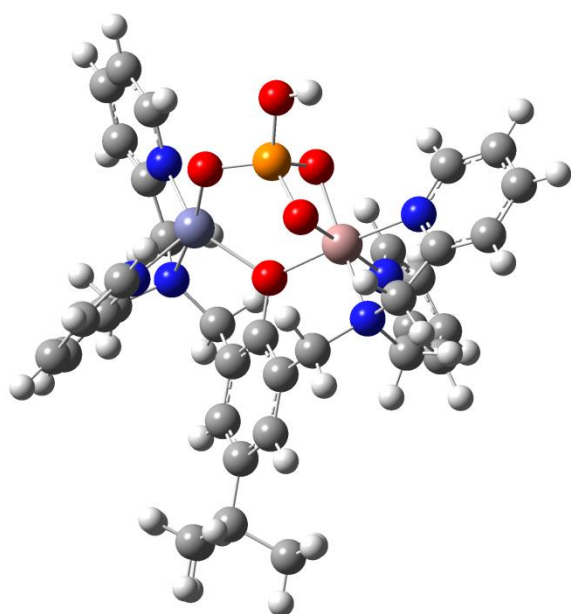
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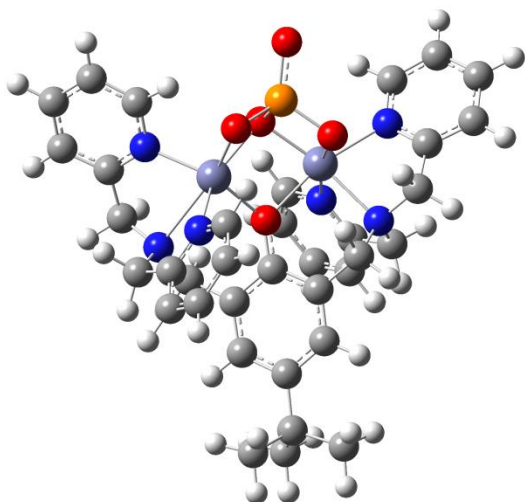
[2]H⁺



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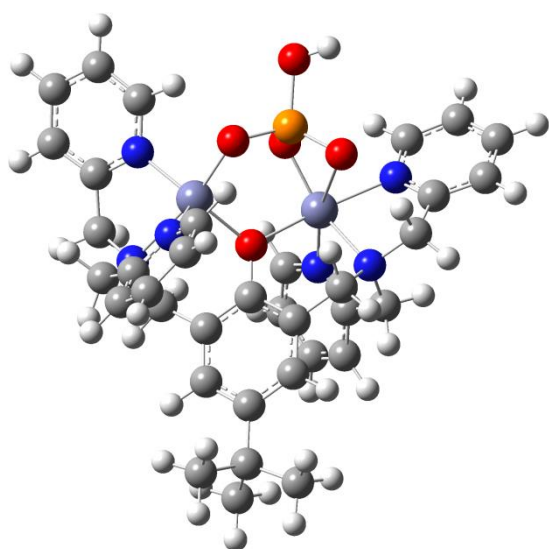
[3]



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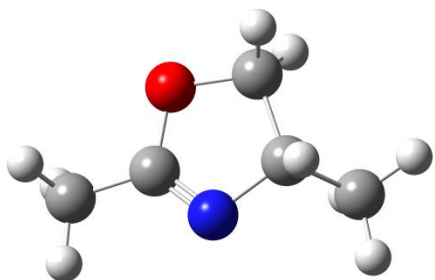
[3]H⁺



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 C,0,-3.8066680662,-0.6412528855,-0.9466910339
 C,0,-4.7839197485,-0.086657358,-1.7786514908
 C,0,-4.5694962248,-0.0662105768,-3.1603177939
 C,0,-3.3852574432,-0.6021499837,-3.6806882657
 C,0,-2.4426839611,-1.128360107,-2.7991552651

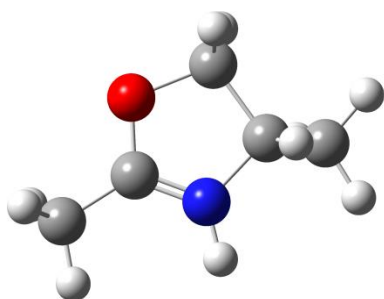
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 H,0,-3.3994932262,2.854037331,1.2823171678
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 H,0,-1.2131611909,-6.7366937682,0.7731483578
 H,0,-0.4785267912,-4.580416771,-0.3305675256
 H,0,-5.6958609641,0.3161008687,-1.3521162263
 H,0,-5.3172266051,0.3588354679,-3.8208840267
 H,0,-3.1942405237,-0.6110521356,-4.7465882462
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 O,0,2.1431020515,-1.269998767,-2.4364969312
 O,0,2.2318143302,-3.9654529884,-1.8600056339
 O,0,-0.086658694,-2.6843464119,-1.5518055317
 O,0,1.8853199686,-2.1022459661,0.1362596139
 H,0,2.974161558,-3.8800184617,-2.4940286816

[4]



C,0,-1.1934877331,-0.2793540618,-1.1750958967
 C,0,-0.6966960614,0.1881496472,0.1453566465
 N,0,-0.7631758027,-0.428685625,1.2702268431
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 H,0,-1.6404166437,-1.2682446684,-1.0697516935
 H,0,-0.888452885,0.6898569704,3.0543207841
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 H,0,-0.3718488441,-0.3237247264,-1.8982441057
 H,0,-1.9393027166,0.4185620149,-1.5710270927

[4]H⁺



C,0,-1.2545102315,-0.2478285888,-1.1996638211
 C,0,-0.725126198,0.2532470687,0.0863296584
 N,0,-0.7896424822,-0.3279407132,1.2661097087
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