Supplementary Material (ESI) for Chemical Communications

COMPUTATIONS

A New Zinc-Zinc-Bonded compound with an α-diimine ligand: Synthesis and Structure of $[Na(THF)_2]_2 \cdot [LZn\text{-}ZnL]$ (L = $[(2,6\text{-}^{i}Pr_2C_6H_3)N(Me)C]_2^{2-}$)

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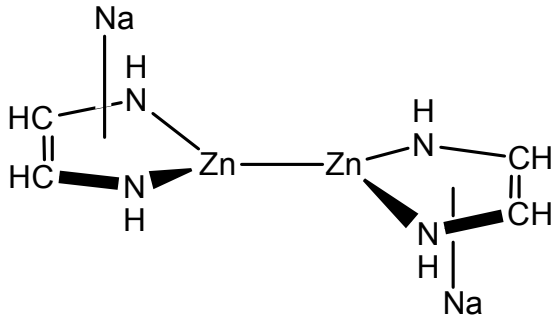
The Model Molecule



Cartesian coordinates

Zn	.622755	-.722791	.705638
Na	.414587	-.372292	3.474998
N	2.230117	-.557023	1.919120
N	.218730	-2.236272	1.981271
C	2.442842	-1.746241	2.648901
C	1.377100	-2.635776	2.681984
H	3.080551	.000503	1.795145
H	-.484117	-2.977650	1.905132
H	3.395649	-1.953426	3.156363
H	1.429804	-3.594744	3.216676
Zn	-.622755	.722791	-.705638
Na	-.414587	.372292	-3.474998
N	-2.230117	.557023	-1.919120
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H	-3.395649	1.953426	-3.156363
H	-1.429804	3.594744	-3.216676

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Theoretical Method

The structure of the model molecule $Zn_2(NH\text{-}CH\text{-}CH\text{-}NH)_2Na_2$ was optimized at the BP86 level of theory with DZP++ basis sets using the Gaussian 94 program (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andes, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94,* Revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995).

The density functional theory (DFT) approach is the BP86 method, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional.[i, ii]

In this work the double-ζ plus polarization (DZP) basis sets used for carbon and nitrogen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(N) = 0.80$ to the Huzinaga-Dunning standard contracted DZ sets and are designated (9s5p1d/4s2p1d).[iii,iv] For Zn, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d).[v,vi] DZP basis set for Na is McLean and Chandler's DZ set plus a set of d functions with exponent $\alpha_d(Na) = 0.175$, and designated (12s9p1d/6s5p1d).[vii]

(i) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(ii) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(iii) Dunning, T. H. *J. Chem. Phys*. **1970**, *53*, 2823
(iv) Huzinaga, S. *J. Chem. Phys*. **1965**, *42*, 1293.
(v) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
(vi) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys*. **1979**, *71*, 705.
(vii) McLean, A. D; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

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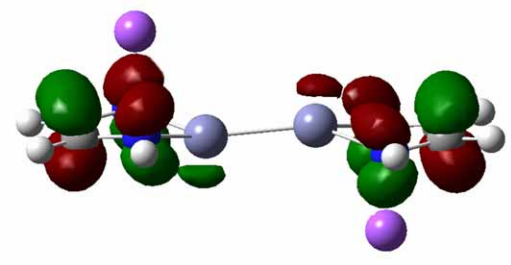
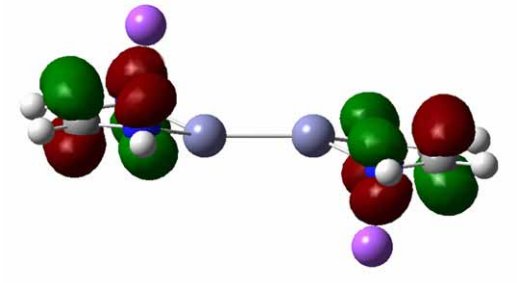
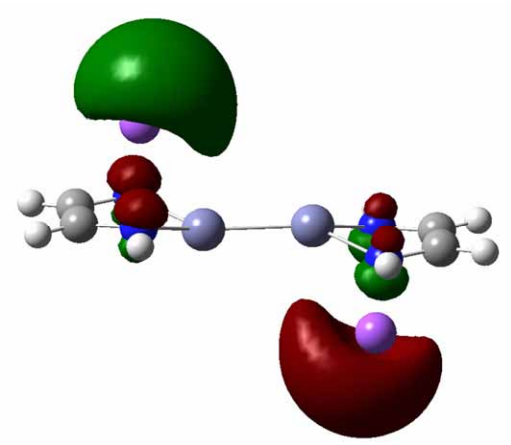
Frontier Molecular Orbitals HOMO-1, HOMO, LUMO, LUMO+1, and LUMO+2.



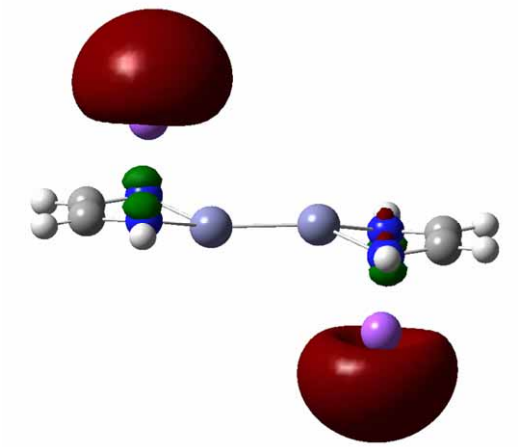
HOMO-1



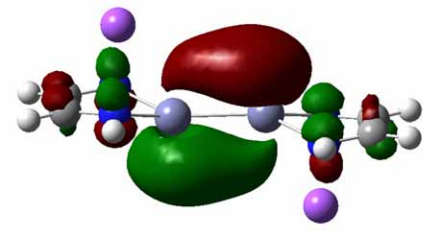
HOMO



LUMO



LUMO+1



LUMO+2