Beryllone: a Novel Divalent Beryllium Lewis Base

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INTRODUCTION

The chemistry of divalent carbon(0) species, or carbones, has recently gained intense theoretical and experimental developments. A highlight of this improvement was the theoretical prediction by Frenking[1] – and further synthesis by Bertrand[2] – of carbodicarbenes, $C(NHC)_2$, as a new type of CL_2 compound. The dative bonds between the ligands and the central carbon atom makes the compound act as a double Lewis base, since the four valence electrons of the central carbon are retained as lone pairs.

In this work, quantum chemical methods have been applied to propose a new class of divalent beryllium(0) species, analogous to carbones, in which the central beryllium atom has one lone pair. The calculations were performed in order to highlight the nature of the Be-L chemical bond, and to obtain thermochemical properties of this novel type of Lewis base.

METHODS

Generalized Valence Bond (GVB) calculations at the perfect-pairing (PP) approach were used to study the nature of the chemical bond in $Be(N_2)_2$, a prototype for the beryllone species. All valence electrons were treated at the GVB-PP level, while the core was described by a Restricted Hartree-Fock wave function. Density functional calculations with dispersion correction were applied to the BeL_2 systems, in order to characterize their structures and stabilities, and to obtain the proton affinities and complexation to BH_3. The classes of ligands comprise different types of N-heterocyclic carbenes and phosphines, as well as CO and N_2. The programs VB2000 and Jaguar were used in this work.

RESULTS AND DISCUSSION

Figure 1 shows some selected GVB-PP orbitals of $Be(N_2)_2$. One could see that the bonding between Be and N is of a dative type, in which the electron pair is oriented from the N to the Be. Figure 1 also shows the beryllium lone pair, evidencing the Lewis base nature of the compound.

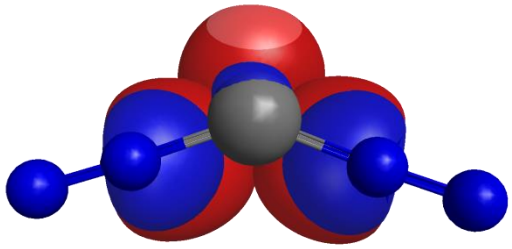

Figure 1. Six valence GVB orbitals of the $Be(N_2)_2$ system, highlighting the dative bonds between Be and N, and the Be lone pair.

For the beryllone compound in which the ligand is an imidazole-2-ylidene, the proton affinity and the ΔG for BH_3 complexation at B3LYP/6-31G** are 319.4 and -32.9 kcal mol^{-1}. In comparison, the respective values for the analogous carbone at MP2/TZVPP//BP86/SVP are 254.2[3] and -26.1[4] kcal mol^{-1}.

CONCLUSIONS

The calculations reveal the nature of the Be-L bonding in beryllone species, and show that it acts as a Lewis base.

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