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On bonding in bis(dimethylglyoximato)nickel(II)

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ABSTRACT

The Ni(II) complex of dimethylglyoxime (dmgH where H is dissociable oxime proton) occurs as an infinite chain of the discrete molecule $Ni(dmgH)_2$ with a Ni—Ni distance of 3.24 Å. Density Functional Theoretical calculations, using LanL2DZ and 6-31+G(2d,p) as two sets of basis functions and M06-2X as the functional, show that the dimeric unit $[Ni(dmgH)_2]_2$ has a cohesive energy more than 20 kcal mol^{-1}. This energy is almost same in the corresponding hypothetical zinc analogue. Since there cannot be any metal-metal bond in $[Zn(dmgH)_2]_2$, possibility of a Ni—Ni bond in $[Ni(dmgH)_2]_2$ is precluded. This is supported by qualitative m.o. analyses also. Further the Ni—Ni bond distance is almost same as the sum of the van der Waals radii of the two Ni atoms as designated by Bondi which is 3.26 Å. It is found that the binding energy in $[Ni(dmgH)_2]_2$ arises from aromatic-aromatic interactions and that in $[Zn(dmgH)_2]_2$ due to π-π interactions between the ligand frameworks. An energy decomposition analysis show that electrostatic and dispersion effects govern the cohesive energy in $[Ni(dmgH)_2]_2$ and $[Zn(dmgH)_2]_2$. Their numerical values are comparable. The orbital interactions in them are relatively less. $[Zn(dmgH)_2]_n$ is not stable for $n > 2$. There are two types of chelate rings in $Ni(dmgH)_2$ monomer – a five membered one with six π electrons and a six membered one having ten σ electrons. Consequently the smaller chelate ring is π-aromatic and the other one σ-aromatic. Such a conclusion is drawn from considerably negative values of NICS(0) (Nucleus Independent Chemical Shift at the centroid of a ring) for the two chelates. The corresponding chelates in $[Zn(dmgH)_2]_2$ are not aromatic.

1. Introduction

Dimethylglyoxime (abbreviated as $dmgH_2$ where H represents the dissociable oxime protons) is much used as an analytical reagent to detect and estimate Ni in the form of $Ni(dmgH)_2$ (Chart 1). A well-known text book in inorganic chemistry [1] writes:

"The high selectivity of" $dmgH_2$ "for the precipitation of Ni^{II} does not result from extraordinarily great stability of the discrete complex, but from the unusual structure in the solid, which leads to low solubility. The planar units are stacked one on another so that the Ni "atoms" are bonded." This haunted us, because according to the m.o. scheme delineated by Cotton [2,3] for $Re_2Cl_8^{2-}$ (Fig. 1), the Ni—Ni bond order in a dimeric unit of $Ni(dmgH)_2$ should be zero since Ni(II) is a d^8 system. Yet it has a large cohesive energy. We have looked into the nature of bonding in $Ni(dmgH)_2$ by means of DFT calculations. For comparison we have studied its zinc analogue also. The results are described here.

2. Computational

All theoretical calculations were performed by using the GAUSSIAN09 suite of programs [4] unless otherwise specified. The functional used uniformly is M06-2X, a nonlocal functional developed by Truhlar [5]. Inputs were usually given from the X-ray crystal structures. In cases of the zinc complexes where crystal structures are not available, Ni was replaced by Zn. For geometry optimizations, two basis sets, LanL2DZ and 6-31+G(2d,p), were used. Basis set superposition error (BSSE), wherever needed, was estimated by using the counterpoise method as implemented in GAUSSIAN09. Nucleus independent chemical shifts (NICS) were calculated by gauge-including atomic orbitals (GIAO) method [6,7] at the M06-2X/LanL2DZ level with the "dummy" atom placed at the centroid of a ring. An Energy Decomposition Analysis (EDA) was carried out by using ADF (Amsterdam Density Functional) package [8] at the B3LYP-GD3(BJ)/TZP level. Single point calculations were done at M06-2X/6-31+G(2d,p) on the optimised geometries at the same level to generate the wave function necessary for Bader's atoms-in-molecules (AIM) calculations, as implemented in AIM 2000 program package [9]. In all calculations spin was restricted, i.e. spin multiplicity was 1.

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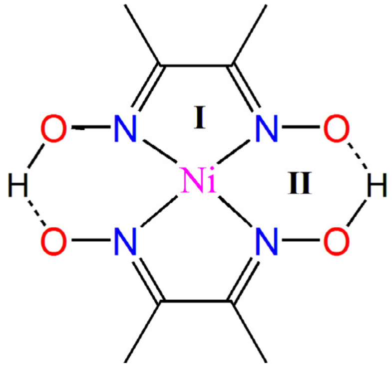

Chart 1. A schematic representation of Ni(dmgH)$_2$.

3. Results and discussion

The X-ray crystal structure of Ni(dmgH)$_2$ has been determined on several occasions [10–15]. The general structure is shown in Fig. 2. It is a one dimensional infinite chain with a Ni-Ni distance [13] of 3.2372 (7) Å. There have been theoretical studies in the past on the discrete single molecule of Ni(dmgH)$_2$ in order to understand the bonding of the oximato ligand with the metal which is dominated by electrostatics [16]. Higher oligomers have received little theoretical attention.

We first consider the dimeric unit [Ni(dmgH)$_2$]$_2$ and then the higher oligomers [Ni(dmgH)$_2$]$_n$. Our M06-2X/6-31+G(2d,p) calculations show that the interaction between two Ni(dmgH)$_2$ units in the dimer is exothermic by 23.59 kcal mol^{-1} (after correcting for BSSE) in the gas phase. This value comes out as 27.40 kcal mol^{-1} at the M06-2X/LanL2DZ level. In order to check whether such a large cohesive energy accrues from any metal-metal bond, we have done the same calculations on the hypothetical molecule Zn(dmgH)$_2$ and its dimer. The reason is that though examples of d^{10}–d^{10} bonding like Ag(I)…Ag(I) are known [17–19], there is no report of bonding between two Zn(II) centers which is also d^{10} but a non-transition element.

From our M06-2X/6-31+G(2d,p) calculations, Zn(dmgH)$_2$ is found to be planar with the sum of the four N-Zn-N angles around Zn is 361.4°. Planar four coordinate Zn(II) complexes are rare. The dimer [Zn(dmgH)$_2$]$_2$ has a staggered conformation (Fig. 3) just like its Ni(II) congener. The distance between the two Zn atoms is 3.43 Å which is slightly longer than the experimental distance between two adjacent Ni centers in [Ni(dmgH)$_2$]$_n$. The stabilization energy ΔE (corrected for BSSE) in [Zn(dmgH)$_2$]$_2$ is found to be 21.43 and 25.51 kcal mol^{-1} respectively at the M06-2X/6–31 + G (2d,p) and M06-2X/LanL2DZ levels. Thus the ΔE's in [Ni(dmgH)$_2$]$_2$ and [Zn(dmgH)$_2$]$_2$ are comparable, which means that there is no metal–metal bond in [Ni(dmgH)$_2$]$_2$, as there cannot be any such bond in [Zn(dmgH)$_2$]$_2$ to hold the two monomeric units together at a distance of 3.43–3.04 Å.

Such a result is in accord with the disposition of the d orbitals described in Fig. 1 which predicts a metal-metal bond order of 0 for a d^8–d^8 dimer. Fig. 1 holds for an eclipsed conformation. But [Ni(dmgH)$_2$]$_2$ is different where the monomeric units are staggered. This precludes the possibility of any δ bonding [20] between the two Ni(II) centers which results from the parallel sideways overlap of the two d$_{xy}$ orbitals. Further, for the same reason, two π bonds (arising out the interactions of d$_{xz}$–d$_{xz}$ and d$_{yz}$–d$_{yz}$) are also not possible. Consequently, Fig. 1 reduces to a situation, where only a head-on overlap of the two d$_z^2$ orbital on the two Ni(II) centers occurs (Figs. 4 and 5a). However, the Ni—Ni bond order is still zero. As expected, the two d$_z^2$ orbitals in [Zn(dmgH)$_2$]$_2$ do not even overlap (Fig. 5b).

Absence of any effective Ni(II)—Ni(II) bond in [Ni(dmgH)$_2$]$_2$ also follows from the magnitude of the Ni—Ni distance of 3.24 Å in the one-dimensional columnar structure. The distance is almost equal to the sum of the van der Waals radius of Bondi [21] for Ni which is

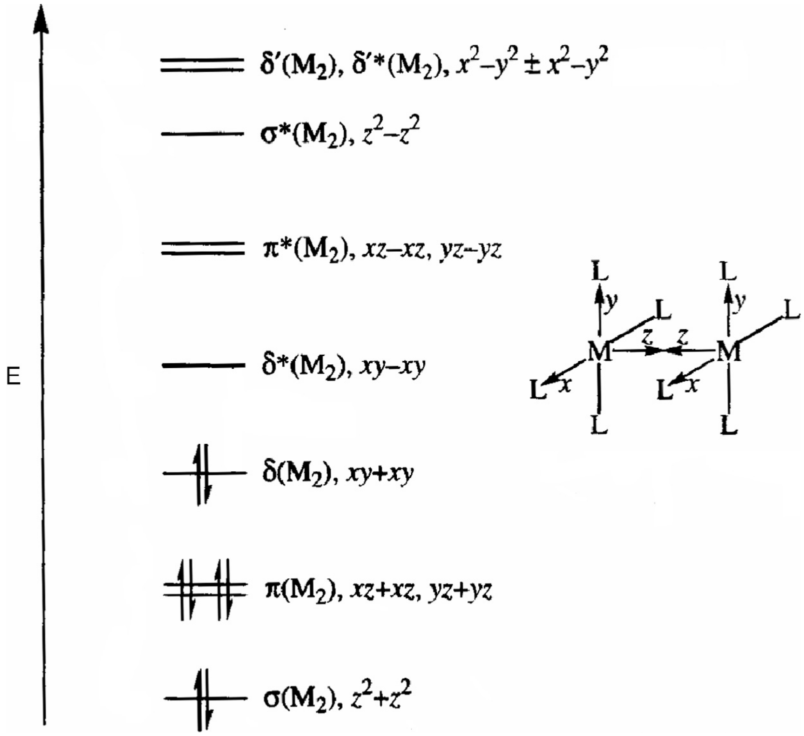

Fig. 1. The qualitative m.o. diagram featuring only the metal d orbitals for Re$_2$Cl$_8^{2-}$ (M = Re and L = Cl$^-$ in the inset) showing a metal-metal bond order of 4. E is energy. The symbols σ, π and δ have their conventional meaning in bonding.