

# 1P094

## Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature

(Kyoto Univ. Fukui Institute for Fundamental Chemistry) Yue Chen, Shigeyoshi Sakaki

**[Introduction]** Activation of dioxygen molecule by the first row transition metals plays crucial roles in biological oxidation. However, the nickel-dioxygen interaction and the role of the nickel center in the relevant dioxygen complexes have been much less investigated than those of copper-dioxygen complexes despite the importance in nickel superoxide dismutase. It is of considerable importance to know how much and why the electronic structure and the bonding interaction of the nickel(I) dioxygen complex are different from and/or similar to those of the copper dioxygen complex. In this work, geometries, bonding nature, and electronic structures of  $(N^{\wedge}N)Ni(O_2)$  ( $N^{\wedge}N = \beta$ -diketiminate), its cobalt(I) and copper(I) analogues, and  $(Ph_3P)_2Ni(O_2)$  were investigated by DFT and MS-RASPT2 methods.

**[Results and Discussion]**  $(N^{\wedge}N)Cu(O_2)$  and  $(Me_3P)_2Ni(O_2)$  take a singlet ground state with a  $C_{2V}$  symmetrical structure and  $(N^{\wedge}N)Co(O_2)$  takes a triplet ground state with a  $C_{2V}$  symmetrical structure. Interestingly, however, the  $(N^{\wedge}N)Ni(O_2)$  takes a  $C_S$  symmetrical structure (Figure 1). In  $(N^{\wedge}N)Ni(O_2)$  with a  $C_{2V}$  symmetry, the first and the second excited states exist slightly above the ground state (Figure 2), whereas the energy gap in other complexes are much larger. More important

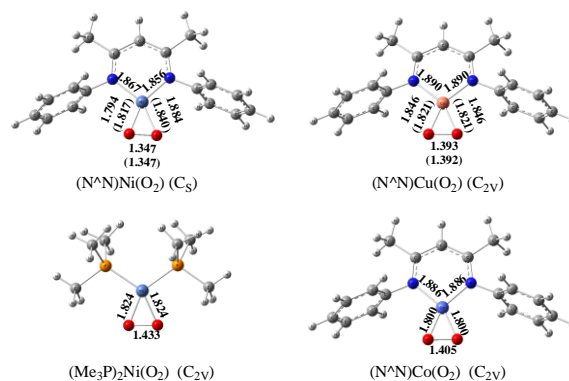


Figure 1. The optimized structures by TPSSPTSS

is that both of the ground and the first excited states in  $(N^{\wedge}N)Ni(O_2)$  belong to  $A''$  irreducible representation under  $C_S$  symmetry, while they belong to different irreducible representations in other complexes. Therefore, the symmetry lowering occurs through the pseudo-Jahn-Teller effect in  $(N^{\wedge}N)Ni(O_2)$  but does not in other complexes.

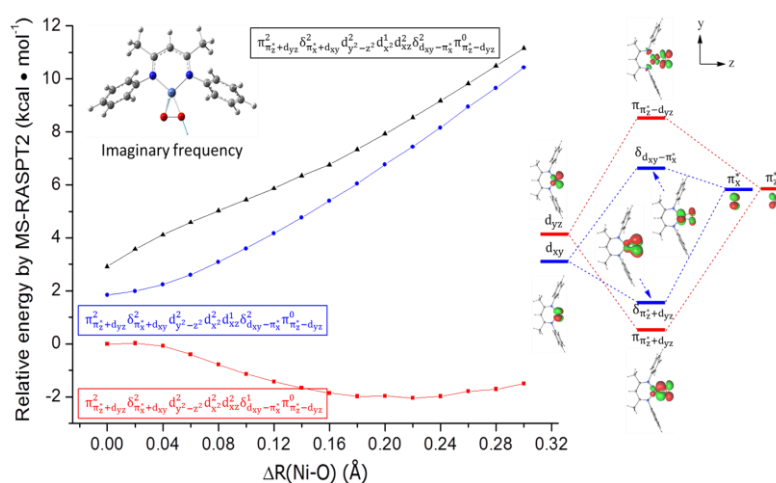


Figure2. MS-RASPT2-calculated potential energy surface.

The population of  $\pi_z^*$  orbital of the  $O_2$  moiety in these complexes is found between 0.96 and 1.14. The total d orbital population is about 7 in  $(N^{\wedge}N)Co(O_2)$ , 8 in the Ni analogue, 9 in the Cu analogue, and 9 in  $(Me_3P)_2Ni(O_2)$ . It is likely concluded that these complexes exhibit a considerable superoxo nature rather than a peroxo nature from the viewpoint of electron distribution. However, little spin density is found on the  $O_2$  moiety in these complexes, while the usual  $\eta^1$ -superoxo complex possesses one unpaired electron on the  $O_2$  moiety.

We introduced a new parameter of M-O distance ( $R_{M-O}^{correct}$ ) in which the difference of ionic radius among Ni(0), Ni(I), Co(I), and Cu(I) was considered. As shown in Figure 3A, the  $R_{M-O}^{correct}$  linearly correlates to  $d_{yz}$  orbital energy ( $\epsilon_{d_{yz}}$ ) in the valence state. Also, we found that the interaction energy ( $E_{INT}$ ) of the  $O_2$  with the metal moiety linearly correlates to the  $\epsilon_{d_{yz}}$  (Figure 3B). Hence, the  $O_2$  binding energy ( $E_{BE}$ ) largely depends on the  $d_{yz}$  orbital energy and the promotion energy ( $E_{prom}$ ) to the valence state; see Figure 3B.

The calculated Gibbs energy barriers ( $\Delta G^\ddagger$ ) of hydrogen abstraction from phenol suggest that

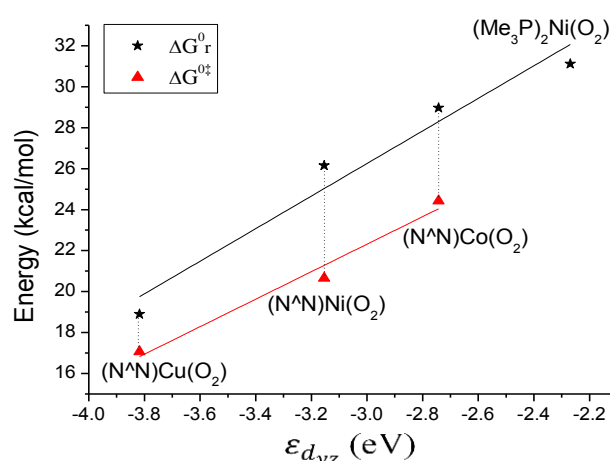
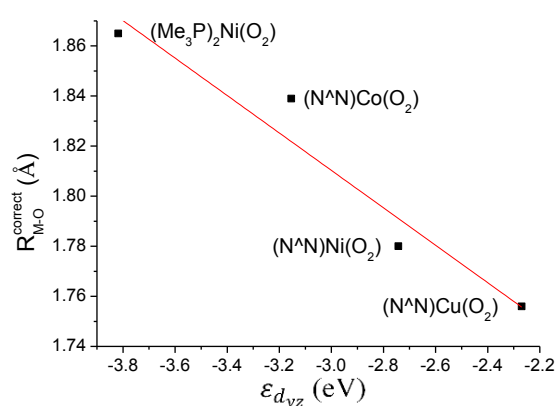
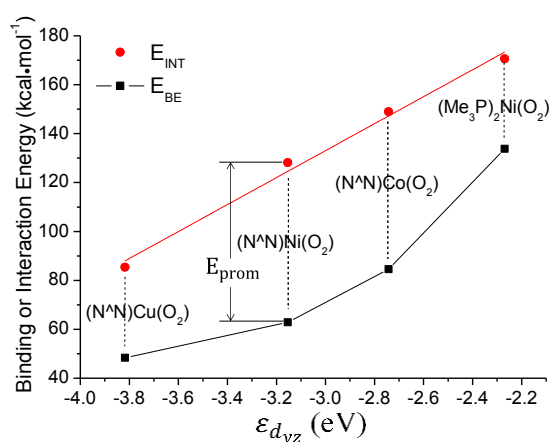


Figure 4. The correlations of  $\Delta G_r$  vs.  $\epsilon_{d_{yz}}$ , and  $\Delta G^\ddagger$  vs.  $\epsilon_{d_{yz}}$ .



(A)



(B)

Figure 3. The correlations of (A)  $R_{M-O}^{correct}$  vs.  $\epsilon_{d_{yz}}$  and (B)  $E_{BE}$  and  $E_{INT}$  vs.  $\epsilon_{d_{yz}}$

$(N^{\wedge}N)Ni(O_2)$  and  $(N^{\wedge}N)Co(O_2)$  are reactive toward phenol but  $(Me_3P)_2Ni(O_2)$  is not. Our computational results also suggest that  $(N^{\wedge}N)Cu(O_2)$  is reactive toward phenol with Gibbs energy barriers of 17.1 kcal/mol. Interestingly, we found the linear relationships between the  $\Delta G^\ddagger$  of hydrogen abstraction and the  $\epsilon_{d_{yz}}$  and between Gibbs reaction energy ( $\Delta G_r$ ) and the  $\epsilon_{d_{yz}}$  (Figure 4). These results indicate that higher  $\epsilon_{d_{yz}}$  leads to a stronger interaction between  $O_2$  and ML, which is not favorable for the reactivity of the dioxygen complex.