DFT Calculations of Cubane-Type $Mo_2Ru_2S_4$ Clusters. Stability of a Possible Dinitrogen Cluster and an Isolable Acetonitrile Cluster

Kazunari Yoshizawa,*[1] **Naoki Kihara,**[1] **Yoshihito Shiota,**[1] **Hidetake Seino,**[2] **and Yasushi Mizobe***[2]

[1]Institute for Materials Chemistry and Engineering, Kyushu University, Higashi-ku, Fukuoka 812-8581

[2]Institute of Industrial Science, The University of Tokyo, Meguro-ku, Tokyo 153-8505

Received April 20, 2005; E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp

The electronic properties of cubane-type mixed-metal sulfido clusters with an $Mo(V)_2Ru(II)_2S_4$ core and possible dinitrogen activation on it are described from DFT computations. The cluster $[(CpRu)_2\{MoCl_2(MeCN)\}_2(\mu_3\text{-}S)_4]$ ($Cp = \eta^5\text{-}C_5H_5$), whose Cp* analogue ($Cp^* = \eta^5\text{-}C_5Me_5$) was isolated and fully characterized by X-ray crystallographic analysis, has a closed-shell singlet ground state. Upon release of the acetonitrile ligands, the ground state remains in a closed-shell singlet state, the corresponding open-shell singlet and triplet states lying $2\,\mathrm{kcal\,mol^{-1}}$ above the closed-shell singlet state. Dinitrogen can hardly coordinate to this neutral $[(CpRu)_2(MoCl_2)_2(\mu_3\text{-}S)_4]$ cluster. However, upon reduction by two electrons the binding energy for two N_2 molecules to the resultant anionic cluster $[(CpRu)_2\{MoCl_2(N_2)\}_2(\mu_3\text{-}S)_4]^{2-}$ increases to $4\,\mathrm{kcal\,mol^{-1}}$. This interaction, which still seems too weak to become isolable, is analyzed in terms of molecular orbitals to increase our understanding of dinitrogen activation by synthetic systems. The HOMO of $[(CpRu)_2(MoCl_2)_2(\mu_3\text{-}S)_4]^{2-}$ is pointing toward missing ligands and can interact effectively with the $\pi_g{}^*$ orbitals of dinitrogen. This orbital might play a role in the binding of dinitrogen.

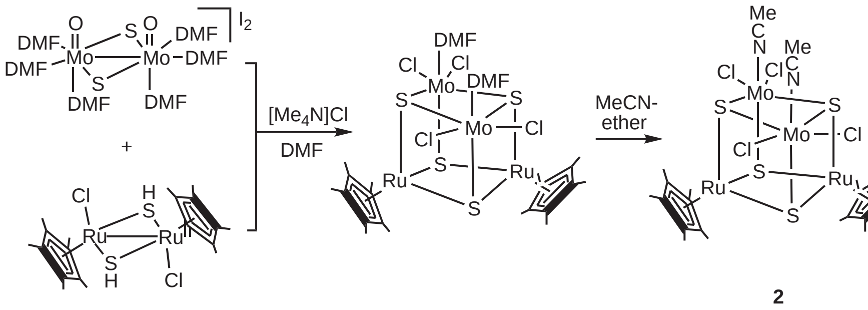
Nitrogenase is an attractive enzyme that can transform the quite inert N_2 molecule into ammonia under ambient conditions.[1] Among the three types of the enzymes, i.e., Mo–Fe, V–Fe, and Fe–Fe nitrogenases, the first type containing the iron–molybdenum cofactor (FeMo-co) as the site for N_2 binding and reduction was structurally characterized by X-ray diffraction in 1992,[2] which revealed the remarkable $MoFe_7S_9$ mixed-metal sulfido core of the FeMo-co. More recently, X-ray analysis at a higher resolution level has disclosed the presence of a single atom at the center of this $MoFe_7S_9$ core, which is presumed to be μ_6-N or less probably C or O, connecting the cuboidal Fe_4S_3 and $MoFe_3S_3$ moieties.[3]

In contrast to this significant progress in the clarification of the FeMo-co structure, the actual binding site and coordination mode of N_2 as well as the mechanism of its transformation into ammonia are essentially unknown, although some results from theoretical studies to address these questions have been documented.[4] The N_2-coordinated metal-sulfido clusters, especially those consisting of the cubane-type or cuboidal metal sulfido cores, may serve as excellent model compounds to elucidate the possible coordination modes and reaction pathways of N_2 at such multimetallic sites with sulfido-rich environments as the FeMo-co. However, despite the isolation of a vast number of homo- and hetero-metallic sulfido clusters relating to the nitrogenase active site to a greater or less extent,[5] well-defined sulfido clusters with N_2 ligands are incomparable. This presents a striking contrast to the fact that a number of stable N_2 complexes with coligands other than sulfides (e.g., phosphines, cyclopentadienyls, amides, and thiolates) have been isolated and structurally characterized, where especially for some Mo and W complexes with tertiary phosphine ancillary ligands transformations of the coordinated N_2 into ammonia, hydrazine, and certain organo-nitrogenous compounds have been demonstrated in detail.[6] Molecular orbital calculations have also been carried out with respect to dinitrogen activation by well-defined metal complexes.[7]

Mizobe and co-workers previously reported the isolation of cubane-type mixed-metal sulfido clusters $[(Cp^*Ru)_2\{MoCl_2(DMF)\}_2(\mu_3\text{-}S)_4]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$, DMF = *N*,*N*-dimethylformamide) from the reaction of $[(Cp^*RuCl)_2(\mu\text{-}SH)_2]$ with $[\{Mo(DMF)_3\}_2(\mu\text{-}S)_2]I_2$ in the presence of $[Me_4N]Cl$.[8] Now it has been found that the recrystallization of **1** from MeCN–ether affords $[(Cp^*Ru)_2\{MoCl_2(MeCN)\}_2(\mu_3\text{-}S)_4]$ (**2**) (Scheme 1). The structure has been determined in detail by single-crystal X-ray diffraction. Since MeCN is isoelectronic with N_2 and one of the nitrogenase substrates, it is of much interest to compare the stability of this MeCN cluster **2** with that of the imaginary N_2 analogue. The results of such a study might provide some clues to the yet unattainable coordination and activation of N_2 at the metal sites of well-defined sulfido clusters. It is noteworthy that with respect to the Mo(0) complexes, *trans*-$[Mo(N_2)_2(dppe)_2]$ and *trans*-$[Mo(MeCN)(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) are both stable and interconversion between these two occurs reversibly; the former is converted into the latter in the presence of excess MeCN in benzene under N_2, while in the absence of MeCN under N_2 the latter returns back to the former.[9]

In this paper, we wish to report density functional theory (DFT) calculations on $[(CpRu)_2\{MoCl_2(MeCN)\}_2(\mu_3\text{-}S)_4]$ (**3**; $Cp = \eta^5\text{-}C_5H_5$), which is a simplified model cluster of **2**, and its N_2 analogue $[(CpRu)_2\{MoCl_2(N_2)\}_2(\mu_3\text{-}S)_4]$ (**4**), together with the results of the X-ray crystallographic analysis and electrochemical measurements of **2**. These may provide a new insight into possible nitrogen activation by synthetic systems.

Published on the web January 13, 2006; DOI 10.1246/bcsj.79.53



Scheme 1.

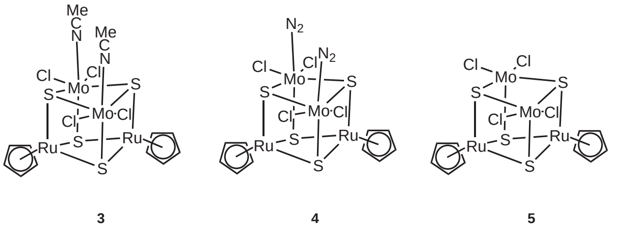


Chart 1.

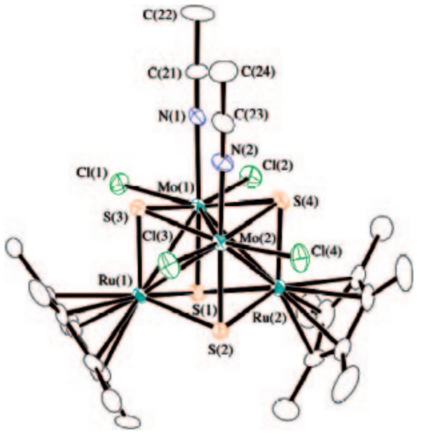


Fig. 1. An ORTEP drawing for **2**. One of the two independent molecules is shown. Hydrogen atoms are omitted for clarity.

Experimental

Method of Calculation. We performed DFT calculations at the B3LYP/LACVP+* level of theory[10,11] on the Jaguar program package[12] to look at the geometries, energies, and electronic properties of **3**, **4**, and their parent cluster $[(CpRu)_2(MoCl_2)_2(\mu_3\text{-}S)_4]$ (**5**) indicated in Chart 1. Complex **5** has open coordination sites at the Mo ions as a result of the release of the MeCN and N_2 ligands. The formal charges of the Cp rings and the chlorine atoms are -1, and that of the sulfur atoms are -2. The formal charge of the Ru ions in these complexes is counted to be $+2$ and therefore they have a closed-shell d^6 configuration, while that of the Mo ions is counted to be $+5$, thus having a d^1 electronic configuration. Our special interest is whether there is a chemical bond between the two Mo ions or not. There are three possibilities for this coupling; the first one is a diamagnetic interaction in which the two units of electron spin in the Mo ions are paired, the second one is an antiferromagnetic interaction, and the third one is a ferromagnetic interaction giving a triplet state. In the diamagnetic species one expects the Mo–Mo distance to be relatively short and can therefore draw a chemical bond between the Mo ions, whereas in both the antiferromagnetic and ferromagnetic species one expects the Mo–Mo distance to be relatively large and cannot draw a chemical bond between the Mo ions. We used the spin-restricted and -unrestricted versions of the B3LYP method to carry out closed-shell singlet, open-shell singlet, and triplet states calculations, which are useful for a better characterization of the coupling between the Mo ions.

Crystallography. Single crystals of **2**•3.25MeCN suitable for X-ray analysis were prepared by dissolving **1**•DMF[7] in MeCN, followed by the addition of ether. A crystal of the dimensions $0.7 \times 0.4 \times 0.2\,mm^3$ was sealed in a glass capillary under argon and data collection was done by a Rigaku AFC7R diffractometer equipped with a graphite monochromatized Mo Kα source ($\lambda = 0.7107\,Å$) at 23 °C. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ-scans; transmission factors: 0.61–1.00). Structure solution and refinements were carried out by using the teXsan program package.[13] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY[14]) and subsequent Fourier synthesis (DIRDIF94[15]), which were refined by full-matrix least-squares techniques with anisotropic thermal parameters. Hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements with fixed parameters. The crystal contains two crystallographically independent molecules, whose structures are essentially identical. Crystallographic data are as follows: triclinic, $P\bar{1}$ (No. 2), $a = 11.685(3)$, $b = 19.230(4)$, $c = 20.337(4)\,Å$, $\alpha = 104.38(2)°$, $\beta = 102.55(2)°$, $\gamma = 93.41(2)°$, $V = 4289(1)\,Å^3$, $Z = 4$, $D_{calcd} = 1.781\,g\,cm^{-3}$, $\mu(\text{Mo K}\alpha) = 1.733\,mm^{-1}$, $F(000) = 2278$, $R = 0.065$, $R_w = 0.087$ for 880 variables and 9781 reflections ($I > 3.0\sigma(I)$) out of 15985 unique reflections ($R_{int} = 0.044$). An ORTEP drawing of one of the two independent molecules of **2** is shown in Fig. 1, while selected bond distances in the two molecules are listed in Table 1.

Crystallographic data for **2** have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-275110. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Electrochemistry. Electrochemical experiments were carried out on a BAS CV-50W electrochemical analyzer using a glassy carbon working electrode and a Pt counter electrode; potentials were referred to a saturated calomel electrode. Cyclic voltammograms of **2** were measured in MeCN containing 0.1 M $[Bu^n{}_4N][BF_4]$ as the supporting electrolyte at the scan rate of $200\,mV\,s^{-1}$.

Table 1. Selected Interatomic Distances for **2**

Molecule **1**			
Ru(1)–Mo(1)	2.855(2)	Ru(1)–Mo(2)	2.856(2)
Ru(2)–Mo(1)	2.848(2)	Ru(2)–Mo(2)	2.861(1)
Mo(1)–Mo(2)	2.821(1)	Mo(1)–N(1)	2.25(1)
Mo(2)–N(2)	2.22(1)	Ru(1)···Ru(2)	3.491(2)
Molecule **2**			
Ru(3)–Mo(3)	2.851(2)	Ru(3)–Mo(4)	2.859(2)
Ru(4)–Mo(3)	2.852(1)	Ru(4)–Mo(4)	2.854(2)
Mo(3)–Mo(4)	2.816(2)	Mo(3)–N(3)	2.21(1)
Mo(4)–N(4)	2.24(1)	Ru(3)···Ru(4)	3.488(2)

Table 2. Computed Total Energies (in hartree) and Relative Energies (in kcal mol^{-1}) of **3**, **4**, and **5** at the B3LYP/lacvp+* Level of Theory

Complex	Closed-shell singlet	Open-shell singlet	Triplet
3	−4409.505929	Not found	−4409.496325
	(0.0)		(+0.4)
	−4408.216065[a]		−4408.202262[a]
	(0.0)		(+8.7)
4	−4363.010175	−4363.006861	−4363.005668
	(0.0)	(+2.1)	(+2.8)
	−4361.772548[a]	−4361.765451[a]	−4361.761517[a]
	(0.0)	(+4.5)	(+6.9)
5	−4143.959525	−4143.960643	−4143.960181
	(0.0)	(−0.7)	(−0.4)
	−4142.843871[a]	−4142.840579[a]	−4142.840136[a]
	(0.0)	(+2.1)	(+2.3)

a) Values of single-point calculations at the B3LYP*/lacvp+* level.

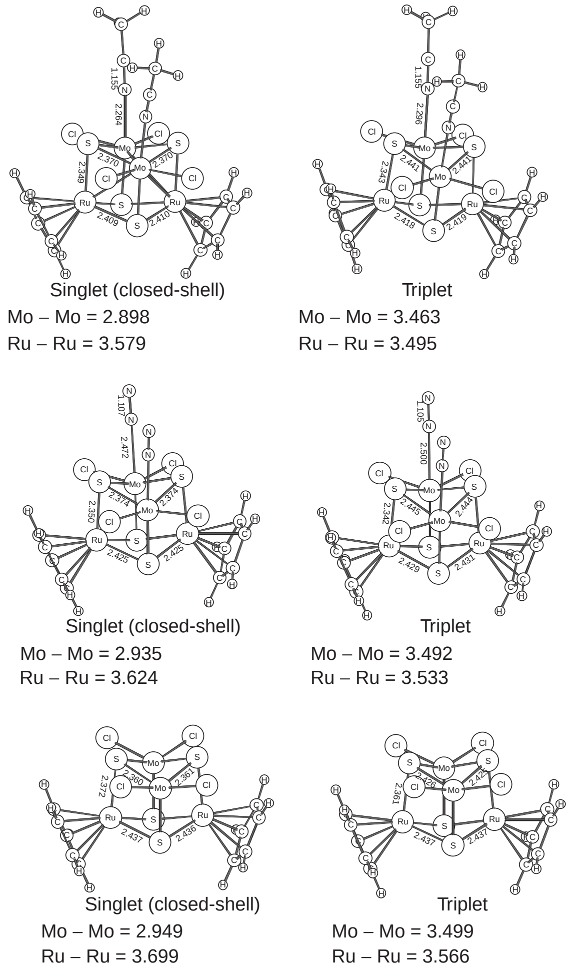


Fig. 2. Optimized structures of the singlet and triplet states of **3**, **4**, and **5** at the B3LYP/lacvp+* level of theory.

Results and Discussion

Magnetic Coupling of the Mo Ions. Table 2 lists computed total and relative energies of **3** and **5**. B3LYP calculations tell us that there is no open-shell singlet state for complex **3**; the closed-shell singlet state lies 0.4 kcal mol^{-1} below the triplet state. Thus, the ground state of complex **3** is the closed-shell singlet state, and therefore we can reasonably draw a bond between the two Mo ions in this state. On the other hand, the open-shell singlet state of **5** lies 0.7 and 0.3 kcal mol^{-1} below the closed-shell singlet and triplet states, respectively. Although the energy difference is small, we can identify from the DFT calculations at the B3LYP level the ground state of complex **5** to be the open-shell singlet state, in which the Mo ions are antiferromagnetically coupled. Naturally, we cannot draw a bond between the Mo ions in this state. In fact, the Mo–Mo distance was optimized to be 2.898 Å in the closed-shell singlet state of **3**, whereas it was optimized to be 3.406 Å in the open-shell singlet state of **5**. Other geometrical parameters such as the Ru–Ru distance and metal–ligand distances, remain unchanged upon the release of the MeCN ligands. For example, the Ru–Ru distances are about 3.5–3.6 Å, the Mo–S and Ru–S distances are about 2.3–2.4 Å, and the Mo–Cl distances are about 2.4–2.5 Å. We carried out additional single-point calculations at the B3LYP* level of theory,[16] which is reported to better estimate relative energies of high-spin and low-spin states in general, using the B3LYP-optimized geometries to look at this conclusion. The closed-shell singlet state is the ground state of complex **5** at this level of theory, as shown in Table 2. Since the B3LYP* method is more reliable in the energy order of different spin states, we tentatively determined the closed-shell singlet to be the ground state of complex **5**. Figure 2 shows optimized structures of complexes **3**, **4**, and **5** in their closed-shell singlet and triplet states.

Figure 3 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the closed-shell singlet state of **3**. The HOMO of **3** is a bonding orbital with respect to the two Mo ions, while the LUMO is an antibonding orbital. The amplitude of the HOMO that is localized well on the Mo ions is fully consistent with the existence of the Mo–Mo bond in this state. Figure 3 also shows the broken-symmetry HOMOs of the open-shell singlet state of **5**. The HOMO(1) and HOMO(2) of **5**, which are derived from a linear combination of the HOMO and LUMO in the closed-shell singlet state, are localized well on the left-side and right-side Mo ions, respectively. Each localized orbital is filled by a single electron in the open-shell singlet state. Computed spin densities at the Mo sites are 1.1 and −1.1, while those at the Ru sites are 0.0.

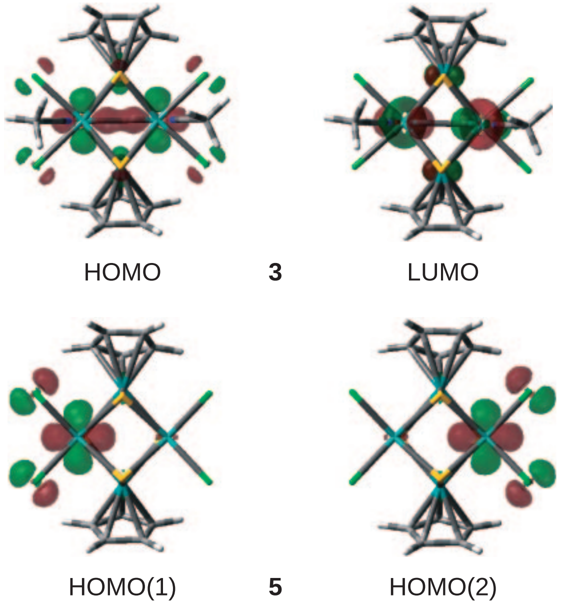


Fig. 3. The HOMO and LUMO of **3** and the broken-symmetry HOMOs of **5**.

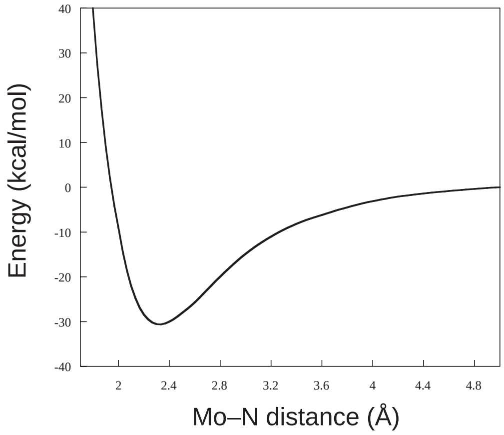


Fig. 4. Interaction energy curve of **5** and two acetonitrile molecules at the B3LYP/lacvp+* level of theory.

Binding of Acetonitrile at the Mo Sites. The ground state of complex **5** is the closed-shell singlet, as shown in Table 2. Since a computed $\langle s^2 \rangle$ value for complex **5** in the spin-unrestricted calculation is 0.983, the broken-symmetry singlet state is spin-contaminated by other spin states such as triplet. Therefore, we used spin-restricted calculations to look at the binding energies of acetonitrile and dinitrogen to this complex. Figure 4 shows a curve of the interaction energy between acetonitrile and complex **5** as a function of the Mo–N distance. A computed binding energy for the two acetonitrile molecules is about 30 kcal mol^{-1} with an Mo–N distance of ca. 2.3 Å. Since this binding energy is not significant, the acetonitrile ligands may be easily released in solution. This result is consistent with the finding that the ^{1}H NMR spectrum of **2** in CD_3CN exhibits the signal of CH_3CN initially bonded to the Mo site at the position of free CH_3CN, indicating that the coordinated acetonitrile in **2** is smoothly replaced by CD_3CN. Unfortunately, since **2** is soluble only in polar solvents and is unstable in common non-coordinating solvents such as CD_2Cl_2, we could not detect the species generated by dissociation of the bonded acetonitrile.

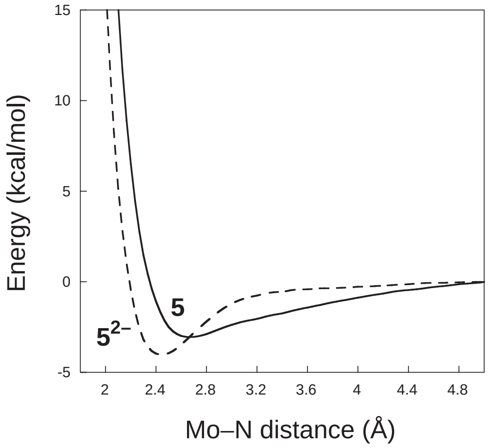


Fig. 5. Interaction energy curve of **5** ($\mathbf{5}^{2-}$) and two dinitrogen molecules at the B3LYP/lacvp+* level of theory.

Possible Dinitrogen Coordination to the Mo Sites. The most important matter in efficient nitrogen fixation is the cleavage of the strong nitrogen–nitrogen triple bond of 225 kcal mol^{-1} under mild conditions. The key to the reductive activation of the triple bond is how to fill the degenerate π_g* orbitals or the high-lying σ_g* orbital of dinitrogen. Let us now look at the interaction between dinitrogen and complex **5** at the coordinatively unsaturated Mo sites. We approached the two dinitrogen molecules to the active sites and calculated the energy with the spin-restricted version of B3LYP. We demonstrate in Fig. 5 a computed interaction energy curve between dinitrogen and complex **5** as a function of the Mo–N distance. This interaction curve is a minimum at 2.7 Å, demonstrating that the interaction is so weak that complex **5** cannot activate dinitrogen effectively. This computational result is reasonable in view of the frontier orbitals of **5** shown in Fig. 6, because there are no filled orbitals that point toward missing ligands at the Mo sites. Such a filled orbital is essential to reductively activate dinitrogen through molecular orbital interactions. Since in the HOMO the two d orbitals at the Mo sites overlap in phase leading to a bonding orbital with respect to the two Mo ions, it is unlikely to play a role in dinitrogen activation.

Although the LUMO of complex **5** is pointing toward missing ligands and can nicely interact with the π_g* orbitals of dinitrogen, it has no electron-donating power because it is vacant. However, if complex **5** accepts a couple of electrons to form the dianion $\mathbf{5}^{2-}$, the former LUMO, which is now fully occupied, can play a role in the reductive activation of dinitrogen through the back donation from the complex. The triplet state of this dianion lies 2 kcal mol^{-1} above the singlet state. Figure 5 shows that the interaction curve between dinitrogen and complex $\mathbf{5}^{2-}$ has a minimum at 2.4 Å, which indicates that the binding of dinitrogen with $\mathbf{5}^{2-}$ is stronger than that with the neutral complex **5**. However, since the binding energy of 4 kcal mol^{-1} for the two nitrogen molecules is still quite small, isolation of the clusters with N_2 ligands is presumably unattainable even from $\mathbf{5}^{2-}$ or its Cp* analogue. It should be noted

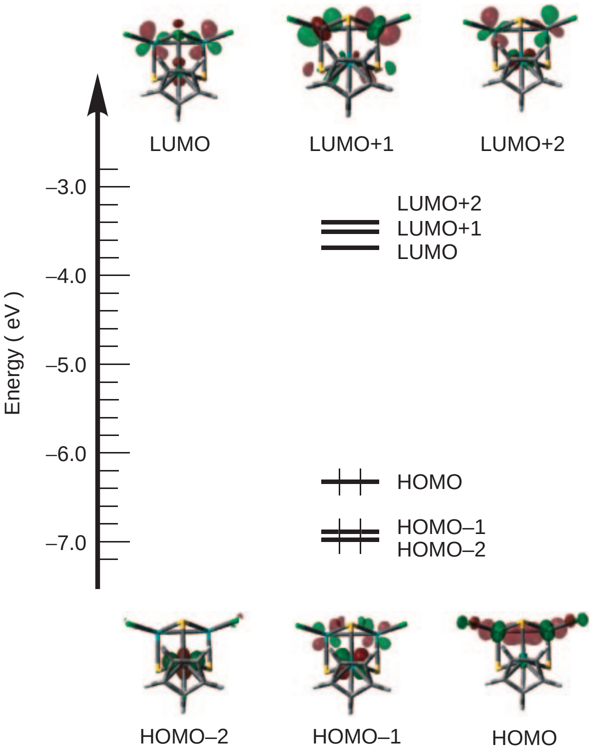


Fig. 6. Frontier orbitals of **5**.

that the change in the geometry and the metal oxidation states of the putative cubane-type $(N_2)MoFe_3S_4$ cluster has also been concluded by extended Hückel MO calculations to facilitate the binding and activation of the N_2 ligand at the Mo site upon reduction by three electrons from $\{(N_2)MoFe_3S_4\}^{3+}$ to $\{(N_2)MoFe_3S_4\}^{0}$.[7e]

Since $[(Cp^*Ru)_2(MoCl_2)_2(\mu_3\text{-}S)_4]$ is not yet available in a stable form, a cyclic voltammetric study was carried out for the acetonitrile cluster **2** dissolved in CH_3CN, which exhibited the presence of two successive reduction waves together with the two successive oxidation processes. However, the former processed at $E_p = -1.17$ and -1.37 V vs SCE are both irreversible, whereas the latters at $E_p = +0.88$ and $+1.04$ V are quasi-reversible. This indicates that the binding of MeCN molecules to the Mo sites in the Cp* analogue of $\mathbf{5}^{2-}$ does not give a stable cluster and might also implicate that the trapping of the N_2 molecule is not attainable for $\mathbf{5}^{2-}$ or $[(Cp^*Ru)_2(MoCl_2)_2(\mu_3\text{-}S)_4]^{2-}$ under these conditions.

Conclusion

We have described using DFT computations the electronic properties of a cubane-type mixed-metal sulfido cluster with an $Mo(V)_2Ru(II)_2S_4$ core and possible dinitrogen activation on it. The $[(CpRu)_2\{MoCl_2(MeCN)\}_2(\mu_3\text{-}S)_4]$ cluster, whose Cp* analogue was isolated and characterized from X-ray crystallographic analysis, has a closed-shell singlet ground state. Upon release of its acetonitrile ligands, the ground state remains to be a closed-shell singlet, the corresponding open-shell singlet and triplet states lying 2 kcal mol^{-1} above the closed-shell singlet state at the B3LYP* level. Although dinitrogen can hardly coordinate to the neutral $[(CpRu)_2(MoCl_2)_2(\mu_3\text{-}S)_4]$, upon reduction by two electrons the binding energy for two N_2 molecules to the resultant anionic cluster $[(CpRu)_2\{MoCl_2(N_2)\}_2(\mu_3\text{-}S)_4]^{2-}$ increases to 4 kcal mol^{-1}. We have considered this weak interaction in terms of molecular orbitals to increase our understanding of possible dinitrogen activation by synthetic systems. The HOMO of $[(CpRu)_2(MoCl_2)_2(\mu_3\text{-}S)_4]^{2-}$ is pointing toward missing ligands and can interact effectively with the π_g^* orbitals of dinitrogen. This orbital might play a role in the binding of dinitrogen.

K.Y. acknowledges the Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the Joint Project of Materials Synthesis of MEXT, and CRET of Japan Science and Technology Agency (JST) for their support of this work. Y.M. also thanks the MEXT and CREST of JST.

References

1 a) B. E. Smith, *Adv. Inorg. Chem.* **1999**, *47*, 160. b) J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965. c) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983. d) R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013. e) B. E. Smith, M. C. Durrant, S. A. Fairhurst, C. A. Gormal, K. L. C. Grönberg, R. A. Henderson, S. K. Ibrahim, T. LeGall, C. J. Pickett, *Coord. Chem. Rev.* **1999**, *185–186*, 669.

2 J. Kim, D. C. Rees, *Science* **1992**, *257*, 1677.

3 O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard, D. C. Rees, *Science* **2002**, *297*, 1696.

4 a) H. Deng, R. Hoffmann, *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 1062. b) I. Dance, *Aust. J. Chem.* **1994**, *47*, 979. c) K. K. Stavrev, M. C. Zerner, *Chem. Eur. J.* **1996**, *2*, 83. d) I. Dance, *Chem. Commun.* **1997**, 165. e) S.-J. Zhong, C.-W. Liu, *Polyhedron* **1997**, *16*, 653. f) P. E. M. Siegbahn, J. Westerberg, M. Svensson, R. H. Crabtree, *J. Phys. Chem. B* **1998**, *102*, 1615. g) T. H. Rod, B. Hammer, J. K. Nørskov, *Phys. Rev. Lett.* **1999**, *82*, 4054. h) T. H. Rod, J. K. Nørskov, *J. Am. Chem. Soc.* **2000**, *122*, 12751. i) T. H. Rod, A. Logadottir, J. K. Nørskov, *J. Chem. Phys.* **2000**, *112*, 5343. j) M. C. Durrant, *Biochemistry* **2002**, *41*, 13934. k) M. C. Durrant, *Biochemistry* **2002**, *41*, 13946. l) I. Dance, *Chem. Commun.* **2003**, 324. m) Z. Cao, Z. Zhou, H. Wan, Q. Zhang, W. Thiel, *Inorg. Chem.* **2003**, *42*, 6986. n) U. Huniar, R. Ahlrichs, D. Coucouvanis, *J. Am. Chem. Soc.* **2004**, *126*, 2588. o) B. Hinnemann, J. K. Nørskov, *J. Am. Chem. Soc.* **2004**, *126*, 3920.

5 See for example: a) F. Barrière, *Coord. Chem. Rev.* **2003**, *236*, 71. b) M. Hidai, in *Perspectives in Organometallic Chemistry*, ed. by C. G. Screttas, B. R. Steele, The Royal Society of Chemistry, **2003**, pp. 62–73. c) M. Hidai, S. Kuwata, Y. Mizobe, *Acc. Chem. Res.* **2000**, *33*, 46. d) R. Hernandez-Molina, M. N. Sokolov, A. G. Sykes, *Acc. Chem. Res.* **2001**, *34*, 223. e) T. Shibahara, *Coord. Chem. Rev.* **1993**, *123*, 73. f) R. H. Holm, *Adv. Inorg. Chem.* **1992**, *38*, 1. g) H. Ogino, S. Inomata, H. Tobita, *Chem. Rev.* **1998**, *98*, 2093. h) *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ed. by E. I. Stiefel, K. Matsumoto, American Chemical Society, **1996**. i) P. Mathur, *Adv. Organomet. Chem.* **1997**, *41*, 243. j) T. Saito, in *Early Transition Metal Clusters with π-Donor Ligands*, ed. by M. H. Chisholm, VCH, New York, **1995**, pp. 63–164. k) I. Dance, K. Fisher, *Prog. Inorg. Chem.* **1994**, *41*, 637.

6 See for example: a) M. Hidai, Y. Mizobe, in *Molybdenum and Tungsten: Their Roles in Biological Processes*, ed. by A. Sigel, H. Sigel, Marcel Dekker, New York, **2002**, pp. 121–161. b) M. Hidai, *Coord. Chem. Rev.* **1999**, *185–186*, 99. c) M. Hidai,

Y. Mizobe, in *Activation of Unreactive Bonds and Organic Synthesis*, ed. by S. Murai, Springer Verlag, Berlin, **1999**, pp. 227–241. d) M. Hidai, Y. Mizobe, *Chem. Rev.* **1995**, *95*, 1115. e) B. A. Mackay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385. f) M. D. Fryzuk, *Chem. Rec.* **2003**, *3*, 2. g) M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200–202*, 379. h) R. R. Schrock, *Chem. Commun.* **2003**, 2389. i) R. L. Richards, *Coord. Chem. Rev.* **1996**, *154*, 83. j) S. Gambarotta, J. Scott, *Angew. Chem., Int. Ed.* **2004**, *43*, 5298. k) S. Gambarotta, *J. Organomet. Chem.* **1995**, *500*, 117. l) G. J. Leigh, *Acc. Chem. Res.* **1992**, *25*, 177. m) M. Hidai, Y. Mizobe, *Can. J. Chem.* **2005**, *83*, 358.

7 a) Q. Cui, D. G. Musaev, M. Svensson, S. Sieber, K. Morokuma, *J. Am. Chem. Soc.* **1995**, *117*, 12366. b) H. Basch, D. G. Musaev, K. Morokuma, M. D. Fryzuk, J. B. Love, W. W. Seidel, A. Albinati, T. F. Koetzle, W. T. Klooster, S. A. Mason, J. Eckert, *J. Am. Chem. Soc.* **1999**, *121*, 523. c) H. Basch, D. G. Musaev, K. Morokuma, *J. Am. Chem. Soc.* **1999**, *121*, 5754. d) H. Basch, D. G. Musaev, K. Morokuma, *Organometallics* **2000**, *19*, 3393. e) F. Barrière, C. J. Pickett, J. Talarmin, *Polyhedron* **2001**, *20*, 27. f) D. G. Musaev, *J. Phys. Chem. B* **2004**, *108*, 10012.

8 H. Seino, T. Masumori, M. Hidai, Y. Mizobe, *Organometallics* **2003**, *22*, 3424.

9 T. Tatsumi, M. Hidai, Y. Uchida, *Inorg. Chem.* **1975**, *14*, 2530.

10 a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785. d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

11 a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724. b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257. c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213. d) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294. e) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654. f) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

12 *Jaguar 5.0*, Schrödinger, LLC, Porland, Oregon, **2002**.

13 *teXsan: Crystal Structure Analysis Package*, Molecular Structure Corp., **1985** and **1992**.

14 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *PATTY: The DIRDIF Program System, Technical Report of the Laboratory*, University of Nijmegen, Nijmegen, The Netherlands, **1992**.

15 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *DIRDIF94: The DIRDIF94 Program System, Technical Report of the Laboratory*, University of Nijmegen, Nijmegen, The Netherlands, **1994**.

16 a) M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* **2001**, *107*, 48. b) M. Reiher, O. Salomon, B. A. Hess, *J. Chem. Phys.* **2002**, *117*, 4729.