

Approaches to rotary molecular motors*

M. Frederick Hawthorne[‡], Bhaskar M. Ramachandran,
Robert D. Kennedy, and Carolyn B. Knobler

*Department of Chemistry, University of California, Los Angeles,
607 Charles E. Young Drive East, Los Angeles, CA 90095-1569, USA*

Abstract: Interest has recently intensified in the search for molecular motors and actuators capable of delivering useful work to nanodevices under the control of electrochemical or photochemical power sources. While many of these man-made molecular machines are designed to deliver rectilinear motion, very few are proposed for the controlled delivery of rotary motion on the time scale characteristic of intramolecular rearrangements. The adaptation of *commo*-bis-dicarbollide metallacarborane structures to the possible design and synthesis of such rotary molecular motors is now under investigation. Progress toward this goal will be reported.

Keywords: metallacarboranes; molecular motors; crystal structures; nanodevices; dicarbollides.

INTRODUCTION AND BACKGROUND

The advent of nanoscience and its resulting influence in chemistry has generated an abundance of totally new chemical enterprises. One of these is the search for controlled molecular motors that can be coupled to nanostructures and employed to affect molecular motion and associated functions. Naturally occurring and man-made molecular motors are well known and frequently reviewed [1]. Two types of motion are commonly represented: linear motion, as in the case of rotaxane structures [2], and rotary motion such as that in enzyme systems [3], and multistep synthetic devices such as those described by Fletcher et al. and Hernandez et al. [4]. While the motional element is a defining characteristic of these molecular systems, an additional variable of equal importance is the characteristic rate of motion and response to external control possible with each structure in a defined environment. Thus, one sees motors that are activated by electron transfer and capable of motion at the speed of molecular rotation and vibration and, at the other kinetic extreme, motors that require several sequential chemical steps interspersed with material separations.

In 2003, the molecular structure of the bis-dicarbollide subset of metallacarboranes suggested their possible use in the construction of redox-controlled rotary molecular motors [5]. Foremost among the possible applications of these species was the nickel bis-7,8-dicarbollide $[\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ structures having formal nickel oxidation states of +2, +3, and +4 (Fig. 1). The $d^8 \text{Ni}^{2+}$ species $[\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ is too easily oxidized by air to be useful in motor construction, while it appeared feasible to consider the transoid $\text{Ni}^{3+} d^7 [\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{1-}$ /cisoid $\text{Ni}^{4+} d^6 [\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ redox transformation as the basis of such a motor that rotates through approximately 180° . The paramagnetic $d^7 \text{Ni}^{3+}$ (transoid) and the diamagnetic $d^6 \text{Ni}^{4+}$ (cisoid) species were originally reported to be interconvertible by a variety of redox reactions, including electrochemical, in 1970 [6].

*Paper based on a presentation at the 12th International Meeting on Boron Chemistry (IMEBORON-XII), Sendai, Japan, 11–15 September 2005. Other presentations are published in this issue, pp. 1299–1453.

[‡]Corresponding author

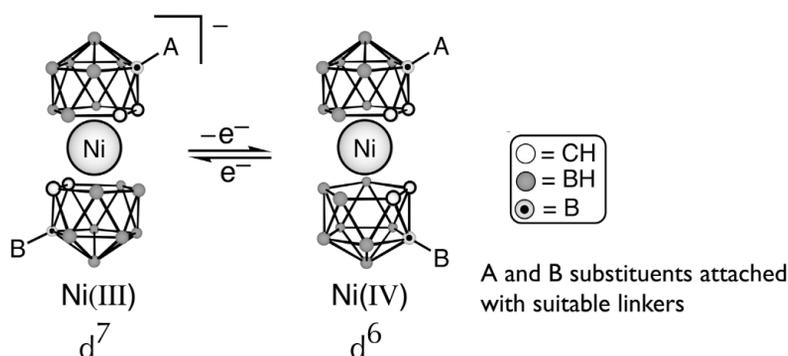


Fig. 1 A rotary molecular motor based on a unique nickelacarborane.

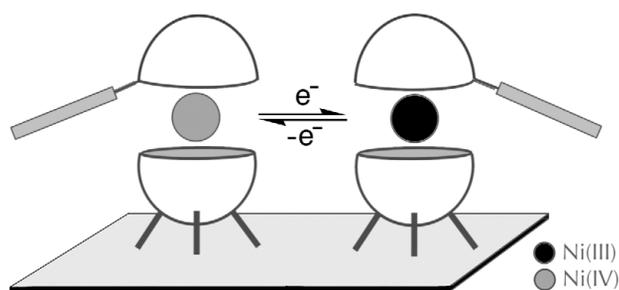


Fig. 2 A graphical representation of the rotary motor.

The idea that the characteristic rotational conformation for each of these two oxidation states persisted in solution at room temperature as well as in the reported crystal structure was strengthened by the observation of a dipole moment of 6.50 D for the Ni^{4+} species in benzene solution, the electrophilic character of this same species leading to crystalline charge-transfer complexes (cisoid Ni^{4+} component) [7] with electron-rich π -systems and anions and the identity of the infrared (IR) spectra of the Ni^{4+} species determined both in solution and the cisoid crystalline state. Later variable-temperature ^1H and ^{11}B NMR studies provide no evidence for the rotation of the two 7,8-dicarbollide ligands present in the Ni^{4+} structure. Evidence to support the transoid Ni^{3+} structure in solution has not yet been obtained, and crystallographic data presented later will confound any conclusion since cisoid, gauche, and transoid structures are observed as the nature and position of the substituent on the 7,8-dicarbollide ligand is varied. Such results are not unexpected, since electrostatic lattice effects and general cumulative van der Waals attractions are intense and any preferential transoid stabilization due to weak molecular orbital interactions could be easily overcome in the crystalline environment (*vide infra*).

Preliminary molecular orbital and density functional theory (DFT) calculations [5] were carried out for the Ni^{3+} and Ni^{4+} unsubstituted bis-7,8-dicarbollide structures. Figure 3 presents the results of total energy vs. dicarbollide rotation for both oxidation states. Figure 4 presents the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) geometrics and energies also as a function of dicarbollide rotation.

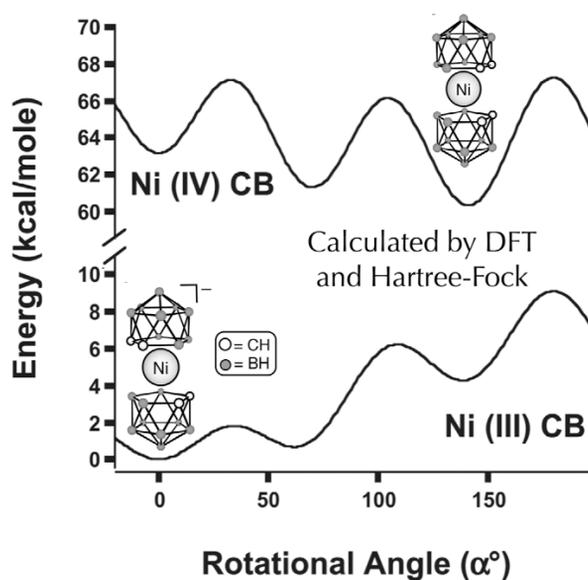


Fig. 3 Total absolute energy of the $(7,8\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Ni(III)}$ anion and $(7,8\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Ni(IV)}$.

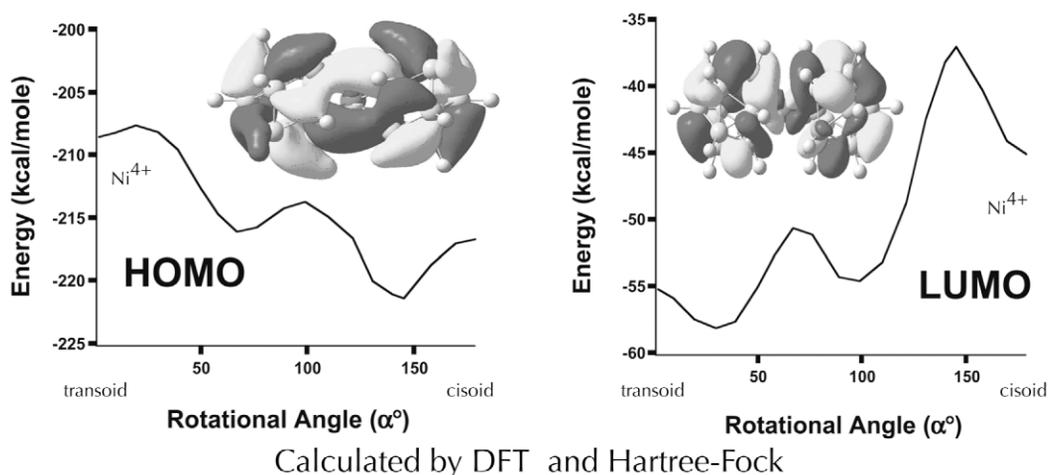


Fig. 4 HOMO and LUMO energy of $(7,8\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Ni(IV)}$ with respect to rotational angle.

As discussed at length in a recent publication [5], the Ni^{4+} HOMO has covalently linked dicarbollide ligands, while the LUMO contains a node at the formal Ni^{3+} center and associated freedom of rotation of the dicarbollides. These two sets of computational results support the observed strong preference of the Ni^{4+} derivatives for cisoid orientation and suggest that the Ni^{3+} derivative may be preferentially stabilized in the transoid configuration. This being so, the simple rotary motor shown in Fig. 2 could become a reality. Furthermore, the manipulation of substituents may provide chiral motors that provide unidirectional rotation specific to both redox steps [5].

TOWARD A MOTOR DEMONSTRATION

The first steps in the demonstration of a rotary motor of the type described here involves the development of synthesis routes to substituted 7,8-dicarbollide ligands, which allow the attachment of desired substituents. Examples of these species are shown in Fig. 5. In these stylized structures the substituent, A, is assumed to be attached to B- and C-vertices by linker chains of predetermined length determined by molecular modeling computations. The desired bis-dicarbollide species are readily obtained by the reaction of the substituted dicarbollide dianions with a nickel salt. Nickel +4/+3 pairs may be interconverted by Fe^{3+} oxidation and NaBH_4 reduction. At the outset, a large number of substituted nickel bis-7,8-dicarbollide derivatives have been prepared with substituents placed in positions 7,(8); 3; 5(6); and 5,6. Figure 6 illustrates three typical $\text{Ni}^{3+}/\text{Ni}^{4+}$ pairs, which demonstrate (as in other examples) a cisoid relationship of cage carbon atoms in the Ni^{4+} oxidation state. However, the corresponding Ni^{3+} derivatives are not exclusively transoid, as expected, but vary between cisoid, gauche, and transoid. Thus, based upon X-ray structures alone, it is impossible to predict the preferred configuration of substituted Ni^{3+} species in solution, although the corresponding Ni^{4+} derivatives are uniformly cisoid. Consequently, further progress with the metallocarborane motor concept will depend upon the configurations of the Ni^{3+} members of each redox pair in solution or attached to a surface. Spectroscopic methods for determining the relative motion of the two dicarbollide rotors will be explored. The first of these involves the structures such as those shown in Fig. 6 in which the 3-substituent, A, is a pyrene molecule attached to the dicarbollide cage using a simple linker chain of optimal length. When this array adapts to a cisoid configuration (Ni^{4+}), the two pyrene π -systems interact to form an excimer dimer [8], which may be observed using its characteristic fluorescence. When the array is reduced to form the transoid Ni^{3+} rotation, this fluorescence, due to intramolecular excimer formation, is lost. This hypothesis is currently under examination.

Successful demonstration of pyrene-pairing in solution could be followed and ordered rotation confirmed by attaching two different, but resonant, fluorescent dyes to the motor structure in place of pyrene. This arrangement would allow the exploration of Forster resonance energy transfer [9] between the dye molecules, a method widely employed in biochemistry. Energy transfer between the two dye molecules varies with distance, and a properly selected dye set should signal the gain or loss of interaction caused by altering the inter-dye distance during cisoid/transoid interconversions.

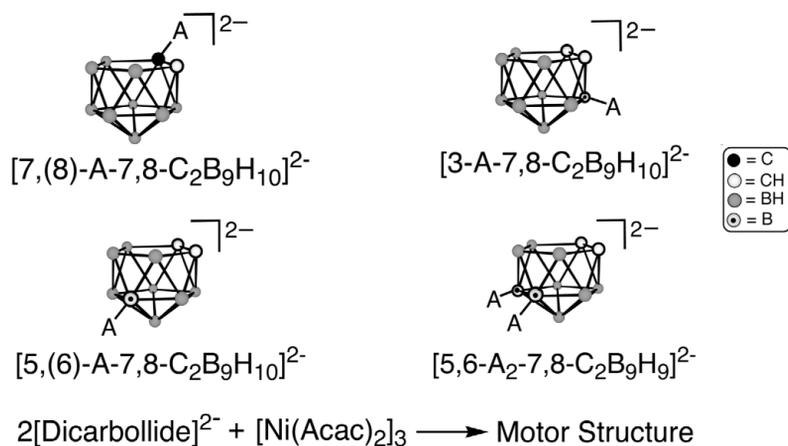


Fig. 5 Substituted dicarbollide ligands for rotary motor.

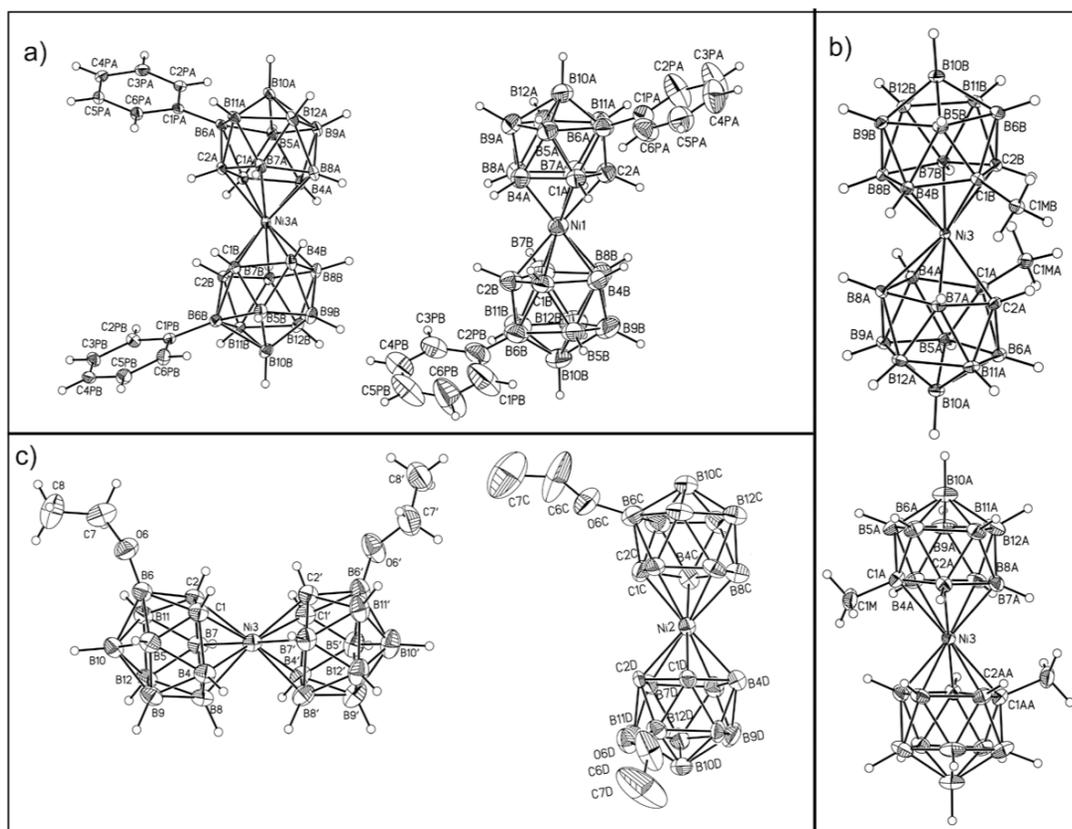


Fig. 6 X-ray diffraction structures of (a) (3-Ph-7,8- $C_2B_9H_{10}$) $_2Ni(IV)$, (3-Ph-7,8- $C_2B_9H_{10}$) $_2Ni(III)^-$; (b) (3-EtO-7,8- $C_2B_9H_{10}$) $_2Ni(IV)$, (3-EtO-7,8- $C_2B_9H_{10}$) $_2Ni(III)^-$; (c) dd(II) [7(8)- CH_3 -7,8- $C_2B_9H_{10}$] $_2Ni(IV)$, dd(II) [7(8)- CH_3 -7,8- $C_2B_9H_{10}$] $_2Ni(III)^-$.

If the solution studies described above are successful, they will be repeated following the attachment of the motor to a solid surface such as sol gel silica [10]. This methodology is now commonly employed in photophysical studies.

AN ADVANCED MOLECULAR MOTOR DESIGN

Assuming that in solution the cisoid configuration prevails for nearly all bis-dicarbollide Ni^{4+} species and that the corresponding Ni^{3+} redox partner is biased toward the transoid configuration by only relatively weak forces, the successful synthesis of the bis-dicarbollide nickel motor may depend upon the enhancement of the stability of the transoid Ni^{3+} rotamers by the introduction of an additional structural feature specific for this purpose. As seen below, this modification of the transoid Ni^{3+} rotamer may be made complementary to the stabilization of the corresponding Ni^{4+} rotamer. The result is an advanced version of the metallocarborene motor design which has noncovalent orthogonal bond stabilization of both the cisoid and transoid motor positions. To accomplish this, use would be made of the strong π -bonding of an aromatic ring with the cisoid Ni^{4+} rotamer and a strong hydrogen bond, which uniquely stabilizes the transoid Ni^{3+} structure. Figure 7 presents the details of such a proposed motor.

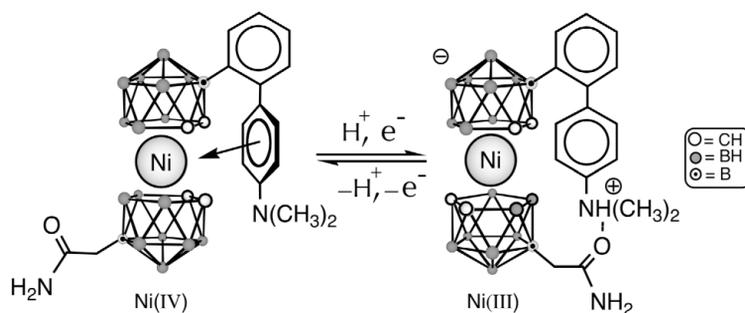


Fig. 7 New motor design with orthogonal noncovalent locks.

Use is made of the known strong charge-transfer bonding of the Ni^{4+} species with 4-dimethylaminophenyl groups [7]. Upon one-electron reduction and protonation, the resulting neutral Ni^{3+} species relaxes this characteristic interaction and the dicarbollide carrying the amide function may rotate to form a H-bond with the protonated dimethylamino group. Synthetic work pertaining to this and other advanced motors is underway.

REFERENCES

1. G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl. *Chem. Rev.* **105**, 1281 (2005).
2. J.-P. Collin, C. Dietrich-Buchecker, P. Gavina, M. C. Jimenez-Molero, J.-P. Sauvage. *Acc. Chem. Res.* **34**, 477 (2001).
3. (a) P. D. Boyer. *Annu. Rev. Biochem.* **66**, 717 (1997); (b) D. Stock, A. G. W. Leslie, J. E. Walker. *Science* **286**, 1700 (1999); (c) W. Junge, N. Nelson. *Science* **308**, 642 (2005); (d) P. D. Boyer. *Nature* **402**, 247 (1999).
4. (a) S. P. Fletcher, F. Dumur, M. M. Pollard, B. L. Feringa. *Science* **310**, 80 (2005); (b) J. V. Hernandez, E. R. Kay, D. A. Leigh. *Science* **306**, 1532 (2004).
5. (a) M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser. *Science* **303**, 1849 (2004).
6. L. F. Warren Jr., M. F. Hawthorne. *J. Am. Chem. Soc.* **92**, 1157 (1970).
7. (a) P. A. Chetcuti, W. Hofherr, A. Liégard, G. Rihs, Günther Rist. *Organometallics* **14**, 666 (1995); (b) D. M. Schubert, D. E. Harwell, C. B. Knobler, M. F. Hawthorne. *Acta Chem. Scand.* **53**, 721 (1999); (c) I. B. Sivaev, V. I. Bregadze. *J. Organomet. Chem.* **614**, 27 (2000).
8. (a) F. M. Winnik. *Chem. Rev.* **93**, 587 (1993); (b) D. Declercq, P. Delbeke, F. C. De Schryver, L. Van Meervelt, R. D. Miller. *J. Am. Chem. Soc.* **115**, 5702 (1993).
9. P. G. Wu, L. Brand. *Anal. Biochem.* **218**, 1 (1994).
10. (a) B. Dunn, J. I. Zink. *Chem. Mater.* **9**, 2280 (1997); (b) S. Chia, J. Chao, J. F. Stoddart, J. I. Zink. *Angew. Chem., Int. Ed.* **40**, 2447 (2001).