II-G Molecular and Electronic Structures of Metallofullerenes

The continued interest in radical ions of fullerenes and metallofullerenes has resulted from the discovery of superconductivity in the CT complexes of alkali metals with fullerenes. Spectroscopic information concerning the electronic and spin states of the metallofullerene has been of great interest and obtained by ESR measurements.

II-G-1 Characterization of Ce@C_{82} and Its Anion

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[*J. Am. Chem. Soc.* **126**, 4883–4887 (2004)]

Ce@C_{82} is isolated by HPLC and the cage symmetry is determined as C_{2v} by measuring the ^{13}C NMR spectra of its anion. The ^{13}C NMR peaks of [Ce@C_{82}]$^-$ show temperature-dependent shifts ascribed to the *f* electron remaining on the Ce atom. Both Ce@C_{82} and [Ce@C_{82}]$^-$ are ESR silent because of the highly anisotropic *g* matrix as well as of the fast relaxation process originating from the orbital angular momentum of the *f* electron. This is the complementary relationship to the observation of the paramagnetic shift in ^{13}C NMR. [Ce@C_{82}]$^-$ has a lower stability in air than [La@C_{82}]$^-$.

II-G-2 Isolation and Crystallographic Characterization of the La@C_{82} Derivative

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[*J. Am. Chem. Soc.* **126**, 6858–6859 (2004)]

The photochemical reaction of La@C_{82} with 2-adamantane-2,3-[3H]-diazirine affords adduct **2**, La@C_{82}(Ad), in a quantitative and highly selective manner. The structure of compound **2** is confirmed by ESR, MS, and UV-Vis-NIR spectroscopies, and the first X-ray crystallographic characterization of an endohedral monometallofullerene derivative is reported. We have reported that the relatively higher reactivity of endohedral metallofullerenes is due to their electronic properties. The reaction EPR spectra reveal the formation of several regioisomers with different La isotopic splittings. In contrast, the regiospecific addition reaction of La@C_{82} with 2-adamantane-2,3-[3H]-diazirine (**1**) affords the first single isomer which has been successfully isolated. Reported here is the first isolation and crystallographic characterization of a paramagnetic endohedral monometallofullerene derivative of the selective La@C_{82} reaction.

II-H High Field and Pulsed Electron Spin Resonance Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of EPR spectroscopy enables us to investigate the heterogeneous and disordered system in detail. Especially the high frequency and pulsed EPR methods achieve the substantial resolution enhancement of spectrum. The advanced EPR spectroscopy is applied to study on the spin state in the heterogeneous system.

II-H-1 W-Band EPR Detection of the Manganese Multiline in the S_2 State of Cyanobacterial Photosystem II Single Crystal

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The multiline signal of the manganese cluster in oxygen evolving complex of photosystem II in the S_2-state was detected in the single crystal form of *thermosynechococcus vulcanus* by W-band EPR measurement.

The distinct 21 lines with irregular spacing were identified, which is due to the hyper fine coupling (hfc) with manganese (I = 5/2) nuclear spins. The combination of the orientation of hfc- and g-tensors among the multisites of manganese cluster strongly affected the appearance of spectrum, and the overlapped hfc structure was smeared out in some orientation of the single crystal. The peculiar spectral patterns in various orientations of the single crystal were well simulated under the assumption of the trimer-monomer structure for the manganese cluster, and the principal values and the direction of the principal axis of an effective g-tensor were determined. The g_z component of the g-tensor was deduced as to be perpendicular to the two-hold axis relating the dimer structure in one subunit of the protein crystal.