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Biomimetic Dinitrosyl Iron Complexes: A Synthetic, Structural, and Spectroscopic Study

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Abstract : Nitric oxide (NO) has become a fascinating entity in biological chemistry over the past few years. It is a gaseous lipophilic radical molecule that plays important roles in several physiological and pathophysiological processes in mammals, including activating the immune response, serving as a neurotransmitter, regulating the cardiovascular system, and acting as an endothelium-derived relaxing factor. NO functions in eukaryotes both as a signal molecule at nanomolar concentrations and as a cytotoxic agent at micromolar concentrations. The latter arises from the ability of NO to react readily with a variety of cellular targets leading to thiol S-nitrosation, amino acid N-nitrosation, and nitrosative DNA damage. Nitric oxide can readily bind to metals to give metal-nitrosyl (M-NO) complexes. Some of these species are known to play roles in biological NO storage and transport. These complexes have different biological, photochemical, or spectroscopic properties due to distinctive structural features. These recent discoveries have spawned a great interest in the development of transition metal complexes containing NO, particularly its iron complexes that are central to the role of nitric oxide in the body. Spectroscopic evidence would appear to implicate species of “Fe(NO)2+” type in a variety of processes ranging from polymerization, carcinogenesis, to nitric oxide stores. Our research focuses on isolation and structural studies of non-heme iron nitrosyls that mimic biologically active compounds and can potentially be used for anticancer drug therapy. We have shown that reactions between Fe(NO)2(CO)2 and a series of imidazoles generated new non-heme iron nitrosyls of the form Fe(NO)2(L)2 [L = imidazole, 1-methylimidazole, 4-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole, and L-histidine] and a tetrameric cluster of [Fe(NO)2(L)]4 (L=Im, 4-MeIm, BzIm, and Me2BzIm), resulted from the interactions of Fe(NO)2 with a series of substituted imidazoles was prepared. Recently, a series of sulfur bridged iron di nitrosyl complexes with the general formula of [Fe(μ-RS)(NO)2]2 (R = n-Pr, t-Bu, 6-methyl-2-pyridyl, and 4,6-dimethyl-2-pyrimidyl), were synthesized by the reaction of Fe(NO)2(CO)2 with thiols or thiolates. Their structures and properties were studied by IR, UV-vis, 1H-NMR, EPR, electrochemistry, X-ray diffraction analysis and DFT calculations. IR spectra of these complexes display one weak and two strong NO stretching frequencies (νNO) in solution, but only two strong νNO in solid. DFT calculations suggest that two spatial isomers of these complexes bear 3 Kcal energy difference in solution. The paramagnetic complexes [Fe2(μ-RS)2(NO)4]-, have also been investigated by EPR spectroscopy. Interestingly, the EPR spectra of complexes exhibit an isotropic signal of g = 1.998 - 2.004 without hyperfine splitting. The observations are consistent with the results of calculations, which reveal that the unpaired electron dominantly delocalize over the two sulfur and two iron atoms. The difference of the g values between the reduced form of iron-sulfur clusters and the typical monomeric di nitrosyl iron complexes is explained, for the first time, by of the difference in unpaired electron distributions between the two types of complexes, which provides the theoretical basis for the use of g value as a spectroscopic tool to differentiate these biologically active complexes.

Keywords : di nitrosyl iron complex, metal nitrosyl, non-heme iron, nitric oxide
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