Distance measurements between two spin labels attached at well-defined sites in proteins by double electron-electron resonance (DEER) spectroscopy have become an established structural tool in Structural Biology. Such measurements are carried out on frozen solutions and provide information on conformational distributions and conformational changes induced by ligand/substrate binding. The standard spin labels used for this purpose are based on nitroxide radicals. In recent years we, and others, have demonstrated the utility of high frequency W-band, 95 GHz) DEER distance measurements in proteins using a new family of spin labels based on Gd(III) chelates. These are particularly useful due to the high sensitivity they have at high magnetic fields. The DEER performance depends on the width of the EPR spectrum, which is determined by the Gd(III) zero field splitting (ZFS) that is a function of the chelate structure, and on the flexibility of the tether used to attach the Gd(III) chelate to the protein. We will present Gd(III)-Gd(III) DEER distance measurements on different protein systems using a variety of Gd(III) tags and will discuss their pros and cons. In addition, we will show that by combining different types of spin labels , like Gd(III), Mn(II) and a nitroxide in the same samples, we can significantly extend the structure information content derived from one sample. Finally we show that owing to the high sensitivity of Gd(III)-Gd(III) distances measurements and the stability of Gd^{3+} chelates, in-cell distance measurements are within our reach. Examples of in-cell Gd(III)-Gd(III distance measurements on Gd Gd(III)-Gd(III labeled ubiquitin and calmodulin delivered into human HeLa cells using osmotic shock and electroporation will be described.