

4.16: Selected Chemistry of Dioxygen, Iron, Copper, and Cobalt

Dioxygen is a powerful oxidant, capable of oxidizing all but the noble metals and of converting many low-valent metal complexes to higher-valent states. As will be detailed in this section, the binding of dioxygen to metals is most usefully considered as an oxidative addition process. The nature of the interaction is determined by the metal, its oxidation state, and its ligands that modulate the redox properties of the metal center. In biological and nonbiological oxygen carriers, several factors allow reversible binding of O₂ to occur, even though this process is metastable with respect to (irreversible) oxidation of the metal, or its ligands, or other species that may be present. Later in this section the bioinorganic chemistry of iron, copper, and cobalt is described. For a wider perspective on the coordination chemistry of these metals, see comprehensive texts on inorganic chemistry.⁵⁶⁻⁵⁸

Many techniques have been used to probe the metal-dioxygen moiety. A summary of these techniques, key concepts, and results is presented in Table 4.3.⁵⁹⁻⁶¹ UV-visible spectroscopy usually characterizes the oxidation state of the metal and in favorable cases the number, geometry, and ligand field strength of ligands. The O—O and M—O stretching modes may be investigated with infrared spectroscopy, provided that the complex is not a centrosymmetric dimer, for then the O—O stretch for the μ -dioxygen species is infrared-inactive. Resonance Raman techniques complement infrared spectroscopy. Not only are the selection rules different in Raman spectroscopy, but a suitable choice of the irradiating wavelength (to coincide approximately with an M-L electronic transition) can amplify those vibrational modes that are coupled, or in resonance, with the electronic transition. This technique is particularly suited as a probe of the metal-ligand environment of metalloproteins, since the many solely protein vibrational modes disappear into background noise. Geometric information on the orientation of the CO moiety with respect to the heme normal has been obtained by examining polarization behavior of infrared bands following photolysis of the Fe—CO bond by linearly polarized light.

Spin and oxidation states of mononuclear iron-porphyrin systems may be assigned directly from magnetic susceptibility measurements and indirectly from Mössbauer spectroscopy. Variable temperature susceptibility measurements are particularly useful for detecting dinuclear systems that share at least one ligand in common if there is **antiferromagnetic** (or ferromagnetic) coupling of the electron spin of one metal center with that of a second.

Definitive characterization of the stereochemistry is usually provided by x-ray diffraction data when single crystals are available. In general, the level of resolution and precision available from protein crystal structures leads to tantalizing uncertainties over the geometry of the M—O₂ species and of the structural changes occurring on oxygenation that are the origin of cooperativity. Precise structural data are more readily obtained from small-molecule model systems. The relevance of these to biological systems is established through congruence of spectroscopic and functional properties. X-ray diffraction techniques also provide important information on the environment beyond the immediate surroundings of the metal center: this information is usually unobtainable from other techniques, although recent developments in two-dimensional NMR spectroscopy can provide this information for diamagnetic systems. Limited information may be obtained with the use of spin labels or, if the metal center is paramagnetic, with EPR techniques.

Two other techniques that selectively probe the immediate environment of the metal center are EXAFS (Extended X-ray Absorption Fine Structure)⁶⁰ and XANES (X-ray Absorption Near-Edge Structure).⁶¹ The former may yield information on the number and type of bonded atoms and their radial separation from the metal center. The latter technique may reveal the oxidation state and, in principle, may yield geometric information, although in its present state of development some interpretations are contentious. Both techniques have the advantage of not requiring crystalline material. The structural information is more reliable if definitive model systems are available for comparison.

X-ray (and, less frequently, neutron) diffraction techniques on single crystals give absolute structural information* and thus provide the basis for interpretation of data obtained from these other techniques that yield relative structural information.

* In favorable situations, sophisticated NMR techniques have been applied successfully to determine the polypeptide folding (e.g., in metallothionein).⁵⁵

Table 4.3: Techniques used to probe the active sites of oxygen carriers

Technique	Abbrev.	Description of Technique	Description of Results

Technique	Abbrev.	Description of Technique	Description of Results
Nuclear Magnetic Resonance	NMR	Quantized orientation of nuclear spin in a magnetic field. Energy separations sampled with radio-frequency radiation.	Identification of histidine by deuterium exchange (N—H vs. N—D) at or near metal, especially if paramagnetic.
Electron Paramagnetic Resonance	EPR	Quantized orientation of electron spin in a magnetic field. Energy separations samples with X- or Q-band microwave radiation.	Location of unpaired electron density from hyperfine splitting by metals or atoms with nuclear spin.
Magnetic Susceptibility		Strength of interaction of sample with magnetic field. Solid state or solution state by Evans' NMR method.	Identification of spin state, spin-equilibria, and spin coupling (ferro- or antiferromagnetic); identification of $\text{Fe}^{\text{III}}\text{—O—Fe}^{\text{III}}$ moiety.
Infrared Spectroscopy	IR	Vibrational modes involving change in dipole moment.	Classification of O—O moiety (superoxo vs. peroxo). Identification of $\nu(\text{M—O})$ and $\nu(\text{M—O—M})$ modes, etc.
Raman and Resonance Raman	R, RR	Vibrational modes involving a change in polarizability. For RR enhancement of modes coupled with electronic transition excited by laser light source.	Complementary to $\nu(\text{O—O})$ and $\nu(\text{M—O})$ especially in metalloproteins. In porphyrins, oxidation and spin state.
UV-visible spectroscopy	UV-Vis	Valence electron transition	Electronic state of metal from d-d transitions. Identification of unusual ligands, e.g., Cu(II)—SR , $\text{Fe}^{\text{III}}\text{—OPh}$, $\text{Fe}^{\text{III}}\text{—O—Fe}^{\text{III}}$. Single crystals and polarized light give geometrical information.
X-ray Photoelectron Spectroscopy	XPS (ESCA)	Inner-shell electron transitions.	Oxidation state of metal.
Mössbauer Spectroscopy		Excitation of nuclear spin by γ rays.	Oxidation and spin state. Antiferromagnetic coupling (Fe only).
X-ray Single-crystal Diffraction		Fourier transform of diffraction data reveals location of electron density.	Precise three-dimensional structure, bond distances and angles for small molecules. Lower resolution and precision for proteins.
Extended X-ray Absorption Fine Structure	EXAFS	Backscattering of x-rays produces interference fringes on absorption curve at energies just greater than metal absorption edge ($K\beta$ transition)	Number, type, and radial distance of ligand donor atoms bonded to the metal.

Technique	Abbrev.	Description of Technique	Description of Results
X-ray Absorption Near-edge Structure	XANES	Similar to EXAFS except that absorption is monitored at energies near and below the absorption edge.	As for EXAFS. May give geometric information

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