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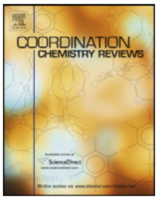

Review

X-ray absorption near-edge spectroscopy in bioinorganic chemistry: Application to M–O_2 systems

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ABSTRACT

Metal K-edge X-ray absorption spectroscopy (XAS) has been extensively applied to bioinorganic chemistry to obtain geometric structure information on metalloprotein and biomimetic model complex active sites by analyzing the higher energy extended X-ray absorption fine structure (EXAFS) region of the spectrum. In recent years, focus has been on developing methodologies to interpret the lower energy K-pre-edge and rising-edge regions (XANES) and using it for electronic structure determination in complex bioinorganic systems. In this review, the evolution and progress of 3d-transition metal K-pre-edge

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Abbreviations: XAS, X-ray absorption spectroscopy; EXAFS, extended X-ray absorption fine structure; DFT, density functional theory; NMR, nuclear magnetic resonance; XANES, X-ray absorption near-edge spectroscopy; Z_{eff}, effective nuclear charge; LMCT, ligand to metal charge transfer; MLCT, metal to ligand charge transfer; EPR, electron paramagnetic resonance; TD-DFT, time-dependent density functional theory; rRaman, resonance Raman; R-TPEN, *N*-alkyl-*N*,*N*′,*N*′-tris(pyridin-2-ylmethyl)ethane-1,2-diamine; 3-^{t}Bu-5-^{i}Prpz, hydrotris(3-tert-butyl-5-isopropyl-1-pyrazolyl)borate; L^8Py_2, 1,5-bis(pyridin-2-ylmethyl)-1,5-diazacyclooctane; 6-Me_2BPMCN, *N*,*N*′-bis((2-methylpyridin-6-yl)methyl)-*N*,N′-dimethyl-trans-1,2-diaminocyclohexane; N_4Py, *N*,*N*-bis(2-methylpyridin-6-yl)-*N*-bis(2-pyridyl)methylamine; H-$PaPy_3$, N-[bis(2-pyridylmethyl)aminoethyl]pyridine-2-carboxamide; TPA, tris(2-pyridylmethyl)amine; 14-TMC, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; 12-TMC, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane; 13-TMC, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane; $S^{Me2}N_4$(tren), *N*,*N*-bis-(2-aminoethyl)-*N*′-(1,2-dimethyl-2-mercaptopropylene)ethane-1,2-di-amine; β-diketiminate, *N*,*N*′-bis(2,6-diisopropylphenyl)-2,2,6,6-tetra-methyl-3,5-pentanediiminato.

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and rising-edge methodology development is presented with particular focus on applications to bioinorganic systems. Applications to biomimetic transition metal–O_2 intermediates (M = Fe, Co, Ni and Cu) are reviewed, which demonstrate the power of the method as an electronic structure determination technique and its impact in understanding the role of supporting ligands in tuning the electronic configuration of transition metal–O_2 systems.

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1. Structure and aim of review

1.1. XAS: an electronic structure determination technique in bioinorganic chemistry

X-ray absorption spectroscopy (XAS) is a powerful geometric and electronic structure determination technique that has found widespread application in bioinorganic chemistry, in particular, to 3d-transition metal systems [1–4]. The unique strength of XAS lies in its element specificity and its applicability to systems in homogeneous and heterogeneous phases. This means that biological samples can be measured in amorphous, crystalline or solution states, including as mixtures and the electronic and geometric structure of each distinct metal and ligand present in the active site of interest can be probed separately, without interference from other elements. In addition to these unique advantages, XAS can be measured on "spectroscopically quiet" elements such as Zn^{2+}, Cu^{1+} and Fe^{2+}, often making it the only spectroscopic technique applicable to systems containing these elements [5]. Traditionally, transition metal K-edge XAS has been used to extract the extended X-ray absorption fine structure (EXAFS) from the spectrum for local geometric structure determination around a metal ion of interest [1,2,4,6–8]. However, over the past 15 years, bioinorganic chemists have also focused on the K-pre-edge and rising-edge region (of 3d-transition metals, together called the XANES region) in order to extract electronic structure information from the system of interest and have extended their spectroscopic toolkit to include metal K- and L- and ligand K-edges [9–13]. This field has been revolutionized by the advent of theoretical methods, which accurately describe the XANES spectra and by cheap and efficient computing power, which allow for fast theoretical calculations on complicated bioinorganic systems [14,15].

The first part of this review will focus on recent advancements in XANES toward understanding and interpreting the metal K-rising-edge and pre-edge region in order to extract electronic and geometric structure information about the bioinorganic site of interest. This review article does not attempt to give a comprehensive list of publications in the field of XAS or XANES, which are numerous; instead a select number of articles showcasing applications of XANES in the field of bioinorganic chemistry are discussed and referenced.

1.2. Application of XANES to M–O_2 intermediates

Mononuclear metalloprotein active sites that activate and/or transport dioxygen typically form an active M–O_2 (M = transition metal) complex in the first step of catalysis. Depending on the system, this first interaction can lead to the formation of a bound O_2, superoxide or peroxide species and correspondingly varying degrees of oxidation at the metal site. Such species have been either shown to exist or implicated in Cu containing proteins including those involved in peptide hormone synthesis such as dopamine β-monooxygenase (DβM) and peptidylglycine α-hydroxylating monooxygenase (PHM) [16,17], and galactose oxidase [16], heme Fe containing proteins such as cytochrome P450, cytochrome *c* oxidase and cytochrome *c* peroxidase [18], a large class of non-heme Fe containing protein involved in oxidation, oxygenation, desaturation and reduction of O_2 to water (see Table 1 in Ref. [19]) [19–21], etc. and Mn containing proteins such as manganese superoxide dismutase (Mn-SOD) [22,23]. Synthetic efforts have been dedicated toward mimicking the structure/function of the transient intermediates generated in the catalytic mechanism of the above-mentioned class of enzymes and in general toward understanding the nature of M–O_2 interactions in transition metal complexes [24–28]. These typically transient or unstable M–O_2 intermediates have been studies using a wide-range of spectroscopic and theoretical tools including synchrotron based XANES and EXAFS techniques. In the second part of this review, recent applications of XANES to M–O_2 (M = Fe, Co, Ni and Cu) containing synthetic systems will be discussed.

2. X-ray absorption near-edge spectroscopy

An X-ray absorption spectrum is obtained when a core electron is supplied with sufficient X-ray energy to be excited to the valence and conduction bands (called the XANES region). In the context of hard X-ray absorption spectroscopy on transition metal complexes, with partially occupied 3d-orbitals, XANES is further subdivided into the "pre-edge" region, which consists of weak, electric dipole-forbidden and quadrupole allowed transitions of the core electrons into valence 3d and charge transfer levels (these weak transitions can gain intensity via d-p mixing, vide infra) and the "near-edge" region which comprise of the rising-edge, white-line and ∼20–50 eV above the white-line (Note that in soft- and tender X-ray absorption spectroscopy (∼250–3000 eV), pre- and near-edge regions are typically treated together).

When the electron absorbs enough energy to overcome the core potential, the resulting photoelectron undergoes a complex array of scattering interactions with the neighboring atoms resulting in the so-called EXAFS region (Fig. 1). This region is used for local geometric structure determination and is very well established in bioinorganic chemistry and several reviews, books and book chapters are available that give a comprehensive description of the technique. Early reviews of the experimental aspects include the chapter by Stern in the book by Koninsberger and Prins, book by Teo and by Iwasawa and articles by Hodgson, and Fonda [1,2,6,7]. Application of EXAFS in the field of bioinorganic chemistry has been described in the book by Solomon and Lever and in review articles by George and Penner-Hahn [5,8,29]. Theoretical advancements in EXAFS have led to development of multiple scattering codes such as FEFF and GNXAS and have been summarized in excellent reviews by Rehr [30–32]. In contrast, a complete quantitative description of the "near-edge" region of the XANES spectrum has not been fully achieved. In this energy range, in addition to a need for proper description of the core hole, long-range multiple scattering contributions become important, which has not yet been addressed completely by theory. In an attempt to bridge this gap, several theoretical packages including FEFF, CONTINUUM, WIEN98, GNXAS, etc. are being used to simulate the near-edge region and to extract local geometric structure information around the absorbing atom with varying degree of success. Recent reviews by J. Rehr presents the current status of XANES theoretical modeling using multiple scattering theory [33–35]. In addition to ab initio multiple scattering programs mentioned above, DFT based methods have also been

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