The electronic structure in 3d transition metal complexes: Can we measure oxidation states?

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Abstract. We discuss the information on the electronic structure that can be obtained by K-shell absorption and emission spectroscopy in systems that contain 3d transition metals. We remind the reader that the chemical sensitivity of the X-ray absorption near edge structure (XANES) is strongly influenced by the local geometry. The X-ray fluorescence is mostly sensitive to the electronic structure and thus complementary to XANES.

1. Introduction

Transition metal compounds are conveniently classified based on the formal oxidation state of the metal ion. The possible oxidation states of an element can be deduced from the electron configuration of a free atom. In a chemical bond it is assigned using simple rules (e.g. oxygen always to -II) and serves the scientist as a guide to infer properties of the compound. For example, a compound that contains Cr in its oxidation VI should not be inhaled because the highly reactive Cr species may cause cancer in the respiratory system. The formal oxidation state also relates to the spin-state and thus to the symmetry of the electronic ground state.

The X-ray absorption near edge structure (XANES) is frequently used to study the metal ion oxidation state. The edge position can be assumed to reflect the local charge density based on screening arguments and/or Coulomb interaction between the valence and 1s electrons. Some technical questions may arise, for example, with respect to the correct way to determine the edge position. This is not subject of this paper. We would like to focus on some other aspects: What is the relation between the formal oxidation state and the actual charge density on the ions in the compound? Connected to that is the question of how to assign electron density to an atom.[1-2] Secondly, how can we measure the charge density? The latter question is addressed in crystallography where a three dimensional electron density distribution is obtained. The theoretical spatial resolution is half of the X-ray wavelength, even
though atomic positions can be obtained with much higher accuracy by fitting routines, and best results are obtained when high quality single crystals are available.

X-ray absorption beam lines at synchrotron radiation sources are able to provide structural information in amorphous or polycrystalline samples but may also reveal some aspects concerning the distribution of the charge density and orbital energy splittings. The change of charge density is indicative of the chemical reaction that takes place at, e.g., the active site of a catalyst. We address in this contribution the problem of studying the electronic structure of 3d transition metal ions by K-shell X-ray absorption and emission spectroscopy.

Spectroscopic techniques are sensitive to the charge distribution also in amorphous samples by measuring energy levels. Optical absorption and electron spin resonance directly probe the electronic structure with some limitations (e.g. dipole forbidden transitions in UV-Vis spectroscopy, diamagnetic systems in ESR). Mößbauer and inner-shell spectroscopies can probe the electronic structure element-selectively. While Mößbauer spectroscopy requires suitable nuclear isotopes, inner-shell spectroscopies have very few limitations with respect to applicability. However, the interpretation of the spectra is complex. Valence shell photoemission presents the most direct means to examine the relevant electron configuration. However, the technique is non-element-selective, surface sensitive and requires high-vacuum conditions even though all these drawbacks can be partly overcome with some experimental effort.

Hard X-ray inner-shell spectroscopies are widely used because they pose fewer experimental challenges. At the K-edge of 3d transition metals the extended fine structure (EXAFS) is a standard tool to characterize the atomic environment. Sophisticated theoretical models have been developed for EXAFS analysis, that are nowadays included in user-friendly interfaces (for a list of programs see http://xafs.org/Software). Interpretation of the near edge structure (XANES) within about 50 eV of the absorption edge has proven to be considerably more difficult resulting in a lively discussing in the scientific community. Recent software developments provide some means to extract structural information from the XANES (see e.g. [3-4]) An analysis can be attempted within a multiple scattering or a molecular orbital framework. Scattering theory treats the absorption process by analyzing the scattering of the photoexcited electron off the neighboring atoms. The photoexcited electron has low kinetic energy and can thus travel far, i.e. it will scatter from several atoms (multiple scattering). Scattering from high coordination spheres will therefore contribute to the XANES spectral shape. The Fermi energy is located just below the lowest experimentally observed excitation which is in non-metallic systems the K pre-edge.

2. Chemical sensitivity of the XANES

The sensitivity of an absorption edge to the electron density is manifold. The intensities and splitting of the spectral features just above the Fermi level, i.e. the K absorption pre-edge, reflect the energy ordering and symmetry of the unoccupied orbitals that are believed to be mainly localized on the metal atom but often hybridize with ligand orbitals or even metal atoms in higher coordination spheres.[5-7] The energy position may be related to the local charge density.[8] The angular momentum of the orbitals that give rise to the pre-edge is mainly d (l=2) (quadrupole transitions) in systems with local inversion symmetry and gains p (l=1) (dipole transitions) contribution when the symmetry is reduced and p-d mixing becomes allowed. The K main edge in 3d transition metals is about 10-20 eV above the Fermi level and arises from transitions into np orbitals (n ≥ 4). It is reasonable to assume that the K main edge position is related to the ionization potential of a 1s electron and it is thus expected to reflect the charge density of the transition metal ion.[9-10] However, the sensitivity is complex and influences from nearest neighbors inter-atomic distances, higher coordination spheres, bond angles, the ligand atomic charges and number of ligands may become visible. All these parameters are
correlated with the charge density and disentangling the various mechanisms that shape the XANES is a formidable task.

Correlations between formal oxidation state and edge shifts have been known since the 1930's. Similarly, correlations between edge shifts and bond lengths have been known for years. Scattering theory predicts a direct influence of edge shifts on bond lengths. An approximate $\Delta E \sim 1/r^2$ edge shift rule has been proposed by Natoli.[11] The local charge density may also influence the energy position of the main edge. De Vries et al. performed a detailed study of the influences of the charge and the Madelung potential on the edge position. They found that both effects have a strong influence.[12]

G. Bunker[13-14] performed scattering calculations of absorption edges of simple molecular clusters in single scattering (using the Müller Schaich formula) and full multiple scattering approximations (using DLXANES [15]). An approach was developed that has the advantage of separating out the effects of chemical charge transfer from the effects of changes in bond length. This is something that is very difficult if not impossible to do experimentally. A power law relation between the average bond length and the formal oxidation state was observed in a series of Mn oxides and KMnO$_4$. The high degree of correlation between these two variables makes it difficult experimentally to determine whether charge state or bond distance is the driving parameter. Fortunately, the theoretical scattering calculations allowed the effects to be separated, because the charge densities were frozen while the atoms were moved. Calculations were also done that involved manually transferring charge, while keeping the distances fixed. Edge shifts were much smaller in this case.

The following conclusions were made for K absorption edges:[13-14]}

- There is a chemical correlation between bond length and oxidation state. It is argued that chemistry and geometrical constraints determine the distance, and the edge position is basically determined by scattering.

- Edges have both single and multiple scattering components. The single scattering is usually dominant, and accordingly the edge shifts measured from states near threshold vary as $1/r^2$.

- If the atoms are held in fixed positions, transferring charge from one atom to the other does not cause large edge shifts. Transferring charge and allowing the atoms to relax to minimize the energy would cause them to move, and in that case the edge position would shift.

Inferring the oxidation state from the edge position is thus not straightforward. If the atoms are free to move and follow the charge distribution, the charge density may be derived from the edge position. If there are steric or crystalline constraints to the motion of atoms it may be unreliable.
Figure 1: Mn K-edge XANES spectra for MnO$_6$ octahedrons with Mn-O distances 2.17 Å (solid line) 2.00 Å (dashed line) and 1.88 Å (short dashed line). The electronic structure of the Mn was fixed in all calculations.

In order to demonstrate the influence of bond distances and metal charge calculations we calculated the Mn K-XANES spectra for MnO$_6$ octahedrons with fixed electronic structure but with different bond distances typical for Mn$^{2+}$ (2.17 Å), Mn$^{3+}$ (2.00 Å) and Mn$^{4+}$ (1.88 Å). The shift of the edge position (we use here the inflection point on the edge) in the theoretical spectra is 2.1 eV for the pair of distances 2.17 Å - 2.00 Å and 1.7 eV for the pair of distances 2.00 – 1.88 Å. The experimentally observed shift of the edge position for Mn(II) and Mn(III) compounds for the spectra (cf. Fig. 4) is 3-5 eV. Therefore, in this case, approximately half of the energy shift can be associated with the effect of bond distance change and half of the effect can be related with the change of the electronic structure.

An interesting and very surprising example, which demonstrates that the position of the edge cannot always be used to determine the oxidation state is a comparison between the Mn(III) and Mn(V) complexes (Fig. 2) [LMn(III)(acac)N$_3$]BPh$_4$ and [LMn(V)(acac)N]BPh$_4$ where L represents 1,4,7-trimethyl-1,4,7-triazacyclononane, acac stands for the 2,4-pentanedionate anion and B$_2$O$_3$Ph$_2$ represents the 1,3-diphenyl-1,3-dibora-2-oxapropane-1,3-diolato dianion as shown in Fig 2. The ligands in these two complexes are the same except for the substitution of the relatively weakly bonded N$_3$ group (bond length is 1.97Å) by strongly bonded N (with bond length 1.51 Å). The average bond lengths for the five other ligands does not change significantly (2.09 Å for Mn(III) and 2.06 Å for Mn(V)).
Figure 2: Schematic representation of [LMn(III)(acac)N3]BPh4 (top) and [LMn(V)(acac)N]BPh4 (bottom) with C (black), O (red), N (blue), B (yellow), Cl (green), H (grey) and Mn (magenta) atoms.

The position of the edge (Fig. 3) is practically the same for these two complexes and this trend is well reproduced in the theoretical calculations of the spectra using the finite difference method.[16] Thus, it is necessary to distinguish two different cases when comparing complexes with different oxidation state: contraction of all distances, which leads to the effects similar to those shown in Fig. 1 and contraction of only one bond. Most of the real cases are usually somewhere between these two extremes. The pre-edge does show the expected increase in intensity with depletion of the 3d shell due to the higher Mn oxidation state. However, the pre-edge intensity is also strongly influenced by the local geometry and is therefore also not an unambiguous marker of the metal oxidation state.
Figure 3: Theoretical (top) and experimental (bottom) Mn XANES corresponding to different oxidation states of Mn: \([\text{LMn(III)(acac)N}_3]\)BPh\(_4\) (black solid) and \([\text{LMn(V)(acac)N}]\)BPh\(_4\) (red dashed).

We show in Fig. 4 the experimental K absorption edges of some model Mn compounds. We compare oxides with coordination complexes for oxidation states II, III and IV. Determining the edge position may be difficult due to the complex spectral shape even though rather robust procedures have been proposed [17]. Experimental artifacts can distort the spectral shape resulting in a large error for the edge position. Alternatively, one can analyze the K absorption pre-edges, i.e. the weak features below the main edge. They also show a complex structure due to orbital hybridization and electron-electron interaction effects but they are believed to be more directly influenced by the charge density. The pre-edges in these systems were analyzed in detail using resonant inelastic X-ray scattering (Fig. 5).[8] This technique gives the energy position along the incident or absorption energy and the energy transfer which is the energy difference between incident and scattered photons. The incident energy is related to the charge density while the energy transfer contains additional information concerning the spin state. It was found that the ordering of the systems along the incident energy yields a reasonable correspondence with the expected charge density: Mn(II) with a 3d\(^5\) configuration is very stable due to Hund’s rule. Thus MnO and Mn(acac)\(_2\)(H\(_2\)O)\(_2\) appear at the same incident energy. For the higher oxidation states the coordination complexes appear at lower energies than the oxides. This is consistent with stronger orbital hybridization and therefore a less positive charge on the Mn ion in the coordination complexes as compared to the oxides.
The spectroscopic results can be compared to calculations of the electronic structure. Multiple scattering codes like FEFF or density functional theory determine the electron density. The calculated electron density can be further treated in order to assign charge to an atom. A population analysis (e.g. Mulliken [18]) distributes the charge density over atomic orbitals. A bond valence analysis is the quantum chemical equivalent to the oxidation state.[19] The different approaches to assign charge to an atom may all yield different absolute values because there are different ways of partitioning the charge. What they have in common is that the charge per atom becomes more complex than the formal oxidation states would suggest. Orbital hybridization leads to non-integer charge fluctuations and the energy position of the spectral feature will flow continuously for different systems. Often this is nicely confirmed in the calculations. It has, for example, been long known that oxygen takes part in the charge transfer and thus cannot always be assigned the charge 2-.[20]
A spectral feature that shows a monotonic behavior as a function of the charge density or the bond valence localized on an atom is suitable as a marker for the bond valence. The K main edge may provide the correct result with the restrictions mentioned before. The example given above for the Mn(III) and Mn(V) complexes can be resolved by concluding that the actual charge on the Mn ion barely changes between the two complexes despite the change in formal oxidation state. A comprehensive study of the K pre-edges has been performed for Fe complexes by Wilke et al.\[21\] However, it is not always easy to separate the weak pre-edge from the main edge resulting in a large uncertainty when determining the energy position. X-ray emission spectroscopy offers an alternative to X-ray absorption and we discuss the chemical sensitivity in the following section.

3. Chemical Sensitivity in X-ray Emission Spectroscopy

X-ray emission is a second order process that occurs after creation of a core hole. We can distinguish between transitions between core levels (Kα, Kβ main lines) and transitions that directly include the valence shell (Kβ valence-to-core).\[8\] Transitions between core levels are promising candidates to separate structural from charge density changes because they are expected to be largely independent of the electronic fine structure (e.g. ligand field splitting) in the valence shell. Their chemical sensitivity arises from either screening effects or electron-electron interactions. The Kβ lines in 3d transition metal ions are dominated by (3p,3d) exchange interactions and are thus sensitive to the valence shell spin state.\[8, 22-23\] If the spin-state is maintained this translates into sensitivity to the charge density. Peng et al. showed that a change in crystal field strength has little influence on the Kβ1,3 spectral shape.\[24\] The X-ray emission can thus be used to disentangle structural from electronic changes.

Figure 6 shows the Kβ lines in Mn oxides and Ni(II) complexes. The charge transfer energy in the Ni complexes has been determined by van der Laan et al. using L-edge spectroscopy\[25\]. The Kβ lines show a monotonic shift with the nominal spin state (Mn oxides) and with the charge transfer energy. In the latter case, a smaller charge transfer energy results in higher charge density on the Ni and a reduced spin state. This means that not all Ni(II) complexes actually have a 3d8 valence shell configuration but that orbital hybridization leads to an ‘effective’ spin on the Ni ions. This charge and thus the spin will change with the type of ligand and the local coordination and does not necessarily follow the formal oxidation state. However, unlike the oxidation state, the charge density is a quantum chemical quantity that can be tracked by experiment.\[26\]
The Kβ main lines arise from transitions between the metal ion 3p and 1s core levels. With increasing emission (fluorescence) energy one approaches the Fermi level and probes the valence shell directly (Kβ satellites or valence-to-core transitions). Transitions between the metal 3d and 1s levels are dipole forbidden and are thus not visible in the spectra. However, dipole transitions from the ligand 2p (3p) and 2s (3s) orbitals to the metal ion 1s shell have a non-negligible strength. Thus, molecular orbitals that are mainly localized on the ligands give rise to the valence-to-core spectrum.[27-29]
Some experimental works aimed at establishing a correlation between oxidation state and emission energies of the Kβ¹ and Kβ₂,₅ satellites.[30-32] Such an empirical description requires measurement of a representative list of reference compounds and is limited to specific systems. The shape of valence-to-core XES during oxidation state change is influenced by two effects: changes of the local structure which leads to the formation of new molecular orbitals and changes of the charge of the metal ion. In order to separate these two effects we have calculated spectra for variations of the Mn(III) compound shown in Fig. 2 changing either only the total charge of the molecule or only the axial ligand.[29] The results are compared to the experimental spectra of the Mn(III) and Mn(V) complexes in Fig. 7. A redistribution of relative intensities between peaks P1 and P2 is observed when the charge on the molecule is increased in the Mn(III) system. Modification of the axial ligand in the Mn(V) complex creates a molecular orbital around –24 eV relative energy which in turn gives rise to a new feature P0 in the XES spectrum. Thus, in this case the valence-to-core XES spectra are sensitive to the formal valence only indirectly via the appearance of new molecular orbitals in the valence band that accompanies the change in oxidation state. Strong orbital hybridization in coordination complexes with low local symmetry may lead to only small differences in the actual charge on the Mn ion when the formal oxidation state changes.

4. Conclusion

X-ray absorption and emission spectroscopy are complementary techniques that, in connection with theoretical modeling, can provide important information on the electronic structure. A simple classification following the formal oxidation state is in many cases not possible. More and more X-ray absorption beamlines at third generation synchrotron radiation sources are providing instruments to record also the X-ray emission. Theoretical codes to model XAS are being modified to include XES. These developments are expected to considerably advance the understanding of the interplay between structural and electronic changes.

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