Cr K-Edge XANES Spectroscopy: Ligand and Oxidation State Dependence – What is Oxidation State?

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Abstract. A series of Cr complexes varying in oxidation state, ligand and geometry were studied with Cr K-edge XANES. The main absorption edge energy shift for an oxidation state change from Cr0 to Cr6+ is found to be similar to that for a series of Cr3+ complexes with different ligands. Theoretical XANES and density of states calculations using FEFF8.0 provided detailed insights in the origin of the XANES features for the series of distorted octahedral CrCl3L complexes. The geometry of the CrCl3L complex governs the position of the main absorption edge. Hard versus soft donor effects are overruled by the chlorine ligand for complexes with a facial geometry, whereas the chlorine ligand does not play a significant role in meridional geometry. The combined results call for a redefinition of generally used concepts like oxidation state.

Keywords: Chromium, XANES, Oxidation State, Geometry, Ligand, Organometallic complexes, Catalysis.

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INTRODUCTION

Detailed X-ray absorption near edge structure (XANES) studies on transition metal complexes have demonstrated the sensitivity of X-ray absorption edges and (pre)edge features to their chemical environment. XANES directly probes the unoccupied density of states (DOS) of the sample and thus gives essential information on the energy and electronic distribution of the molecular orbitals probed. Recent studies show that by carefully observing and analyzing the XANES spectra in combination with theoretical calculational methods, detailed electronic and structural information can be obtained, e.g. the amount of charge redistribution and thus covalent interaction between catalyst and substrate [1].

Organometallic Cr complexes are well-known in homogeneous catalysis [2]. In this study the Cr K-edge XANES is studied for a series of reference materials and a series of organometallic complexes, i.e. as a function of oxidation state and ligand/coordination environment. The position of the absorption edge is shown to be highly sensitive to its ligand surroundings and geometry. Complexes with formally different oxidation states on the other hand can show similar XANES features and positions. The observed results are explained using FEFF8.0 calculations.

EXPERIMENTAL AND THEORY

Chromium K-edge XAFS spectra were measured at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, beamline BM26A (DUBBLE). A double crystal Si(111) monochromator was used. The measurements were performed in transmission mode using optimized ion chambers as detector. To decrease noise, three scans were averaged for each sample.

The FEFF8.0 [3] code was used to perform ab-initio self-consistent field, real space, full multiple scattering calculations. The calculations were performed using the Hedin-Lundqvist exchange correlation potential. A core hole is included in order to mimic the final state of the photon absorption process. Neither E0 nor experimental resolution corrections have been applied. The absorption XANES data and the density of states (DOS) are calculated for selected samples, using their crystallographic and/or the EXAFS data obtained.

RESULTS AND DISCUSSION

Figure 1 displays the representative normalized XANES data for selected Cr complexes with different oxidation states and/or ligand surroundings. Multiple pre-edge features are observed which originate from and are indicative of the complex geometry, i.e hybridization of orbitals (partially) allowing dipole
forbidden transitions [1,4]. The quality of the data is high, providing more detailed XANES as compared to similar [4].

All peak positions are determined by taking the second derivative of the normalized XANES data. In this manner all peaks are easily recognized and the exact positions of the different contributions are obtained, which directly correlate to the positions of the individual (empty) orbitals probed [1]. The last edge contribution, before the first absorption maximum of the absorption edge is reached, is chosen as the main edge. Theory shows that this peak corresponds to the main $1s \rightarrow 4p$ dipole allowed transition for the complexes studied here (vide infra).

FIGURE 1. Normalized XANES spectra for selected reference samples with different oxidation state and ligand.

FIGURE 2. The position of pre-edge and edge features for a series of materials with a range of oxidation states.

The positions of the main adsorption edge and all pre-edge and edge features are plotted in Figure 2. The complexity of Figures 1 and 2 shows that the information is difficult to unravel. In this paper we will focus on the (main) absorption edge position dependence.

For the ‘oxidic’ Cr materials a large increase in edge position of ~9 eV with Cr oxidation state is evident, comparable to previous results [4]. Changing the number of organic and/or electronegative ligands and thereby changing the geometry around the Cr, however, leads to both up- and downwards shifts.

A broad range of Cr(III) samples was studied in more detail and their edge positions are displayed in Figure 3. Within one Cr oxidation state (3+), an increase in edge position of ~8 eV was observed, comparable to that between Cr(0) and Cr(VI) with ‘oxidic’ ligands.

Electronegativity of the ligand, i.e. in this case from Cl to O²⁻, is an important factor for the edge energy difference between the CrCl₃ and Cr₂O₃ [4]. However, this does not account for the broad series of organometallic CrCl₃(L) complexes in which there is an edge shift of ~4 eV is observed. The ligand L within this series consists of different contributing atoms in different combinations. For example, the CrCl₃([9]-aneS₃) complex and the CrCl₃([9]-aneN₃) complex, display a very similar edge energy whereas the Cr is either directly coordinated to 3 S or to 3 N atoms (with very different electronegativities). At the same time the CrCl₃(SNS-decyl) complex edge energy is ~3 eV higher than both the mentioned N₃ and S₃ ligand complexes (SNS-decyl = (HN(CH₂CH₂SC₁₀H₂₁)₂)). The difference between hard and soft donor ligand thus does not explain the results obtained.

FIGURE 3. Main Cr K-edge XAFS edge position as a function of Cr(III) ligand.

Theoretical FEFF8.0 calculations were performed for structurally known complexes. Reference structures like Cr₂O₃, Cr metal, CrCl₃ and CrCl₃(THF)$_3$ confirm the simulation procedure including the potential used. Although the relative main edge positions are not predicted accurately (the muffin-tin approach is known not to be fully adequate for these types of complexes [1a, 4]), all XANES features are nicely reproduced, including the energy difference

FIGURE 4. fac-CrCl₃([9]-aneS₃) (left) and mer-CrCl₃(PNP)(THF) (right).
between the different (pre-) edge features. The simultaneously calculated DOS provides insights in the origin of the different XANES contributions. Here, the DOS results of two representative complexes with a relatively low and high absorption edge energy are discussed, i.e. CrCl_{3}([9]-aneS_{3}) and CrCl_{3}(PNP)(THF) (PNP = \{(isoPr)N(PPh_{2})_{2}\}) (Figure 4).

Figures 5 and 6 present the DOS of the CrCl_{3}([9]-aneS_{3}) and CrCl_{3}(PNP)(THF) resp., with the negative 2nd derivative of the normalized XANES. FEFF8 calculated a Fermi level $E_F$; below $E_F$ the occupied and above $E_F$ the empty molecular orbitals can be found.

**Figure 5.** DOS for the fac-CrCl_{3}([9]-aneS_{3}).

**Figure 6.** DOS for the mer-CrCl_{3}(PNP)(THF).

Cr K-edge XAFS primarily probes the 1s→4p transition (empty DOS), as can be seen from the Cr p DOS and the negative 2nd derivative spectrum. For the CrCl_{3}([9]-aneS_{3}) the Cr p is overlapping with the Cr d, S p and Cl p, indicating that these ligands are reflected in the main edge contribution. For the CrCl_{3}(PNP)(THF) the Cr p is lining up with the P p and N p and no significant overlap with the Cl ligand is observed. The calculated charge transfer for Cr and Cl is large for the 1st complex, whereas negligible charge transfer values for Cr and Cl are observed for the 2nd one.

The DOS plots indicate that geometry is governing the absorption edge position for these Cr^{III}Cl_{3}(L) complexes. Comparing the absorption edge results with the geometry of the complexes, a clear distinction can be made. All ‘low energy’ complexes have a *facial* (fac) geometry, whereas all high energy complexes obtain a *meridional* (mer) geometry (Figure 4). The results presented here indicate that in a fac geometry, i.e. chlorine opposite to ‘neutral’ ligand, chlorine is overlapping with Cr p, with a large charge transfer, and thus overruling the effect of ligand L. This immediately explains why similar energies are obtained for very different L ligand systems. For the mer complexes only L is contributing to the Cr K-edge absorption edge. A reason for this is likely the higher local symmetry of these fac complexes ($C_{3v}$ vs $C_{2v}$).

The empty $t_{2g}$ molecular orbitals are identical and consist of both Cl and L DOS. For mer complexes the $t_{2g}$ orbitals consist of different contributions L and Cl and will therefore be positioned at different energies. XANES probes the lowest $t_{2g}$ level consisting of mainly L. Further density functional theory calculations should provide more information on the molecular orbital diagrams.

**CONCLUSIONS**

Absorption edge energy shifts for an oxidation state dependent series is in the same region as for a ligand dependent series. The large peak shifts observed in a series of comparable Cr^{III}Cl_{3}(L) complexes are shown to be governed by ligand geometry. These results clearly demonstrate that it is impossible to determine oxidation states of unknown complexes by simple scaling their edge positions and emphasize the necessity of redefining the terminology for ‘oxidation states’ of materials and complexes.

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**REFERENCES**

