

ELECTRONIC STRUCTURE OF Ir-HALIDES FROM CHLORINE K-EDGE X-RAY ABSORPTION SPECTROSCOPIC MEASUREMENTS

Robert K. Szilagy^{1,*}, Seiji Mori,² Kenji Hara³, Tomohiro Iwai⁴, and Masaya Sawamura⁴

¹Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT, 59718, USA

²Department of Chemistry, Faculty of Science, Ibaraki University, Mito, Ibaraki, 310-8512, JAPAN

³Catalysis Research Center, Hokkaido University, Sapporo, Hokkaido, 001-0021, JAPAN

⁴Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido, 060-0810, JAPAN

X-ray absorption spectroscopic technique has been proven to provide direct experimental information about the electronic structure of metalloprotein active sites and corresponding biomimetic coordination compounds with relevance to molecular understanding of structure/function relationships. The given study extends the current knowledge and application of ligand K-edge measurements to iridium-containing, homoleptic chloride complexes as a first step of using this spectroscopic techniques for monitoring the electronic and geometric structural changes along a reaction coordinate of iridium-catalysed catalytic reactions. The experimental Ir-Cl bond covalency can also be used to evaluate the performance of modern density functional theory calculations and thus contribute to accurate theoretical representations of catalytic mechanisms.

1 Introduction

Iridium compounds manifest a remarkable homogeneous reactivity in hydrogenation,¹ CO₂ activation,² C-H,^{3,4} C-C bond activation.⁵ These processes often start from structurally and compositionally well-defined pre-catalysts that are transformed to reactive intermediates within the catalytic cycle. Molecular level understanding of the activation of pre-catalysts, the conversion steps between experimentally accessible intermediates and formation of transient species would be a significant aid in rationalized catalyst design.

A similar approach has already been considered for homoleptic chloropalladium complexes.⁶ It was shown that chlorine K-edge X-ray absorption near-edge spectroscopy (Cl K-XANES) is a powerful means of obtaining information about Pd-Cl bonding. In addition, the complementarity of Pd L- and Cl K-XANES analyses was proposed as a fruitful approach to quantitatively evaluate pre-edge and rising-edge spectral features for obtaining metal-ligand covalency and ionic character of bonding, respectively.

The fundamental principles of the quantitative analysis of Cl K-XANES have been developed for a series of chloride complexes.⁷ The key relationship for connecting experimental integrated peak intensities with electronic structure features is the transition dipole expression shown in Eq.(1):

$$D_0 = \frac{1}{3} \frac{h}{N} \alpha^2 I(\text{Cl } 1s \rightarrow 3p) \quad (1)$$

where D_0 is the normalized, integrated pre-edge intensity (eV), h is the number of electron holes probed, N is the number of chlorine absorbers per molecule, and the 1/3 factor is due to angular part of the transition dipole expression for $1s \rightarrow 3p$ excitations. The term $I(\text{Cl } 1s \rightarrow 3p)$ was considered as an empirical transition dipole integral, a proportionality factor connecting D_0 and the chlorine $3p$

atomic orbital character per electron hole (α^2) present in an experimentally probed, unoccupied frontier molecular orbital. The initial value for the $I(\text{Cl } 1s \rightarrow 3p)$ was developed for the terminal chloride ligand donation in Cs_2CuCl_4 ,⁷ which has also been determined by numerous independent spectroscopic techniques and has been shown to be transferable in many terminal chloride ligand containing systems.⁸⁻¹⁰ It is important to highlight that the Cl K-edge XANES study for the chloropalladium complexes⁶ indicated that bridging chloride ligands will require a different transition dipole expression given their different covalent interactions with two neighbouring transition metal ions that the terminal chloride ligand.

In this report, we present our results for two structurally and compositionally well-defined hexachloro iridium(III) and iridium(IV) complexes. These will be the analogous examples to the palladium complexes that will provide us with a unique opportunity to develop the quantitative ligand K- and metal L-edges for catalytically relevant iridium complexes similarly to a recently reported multi K-edge X-ray absorption study on Fe-S-CO complexes.¹¹

2 Experiment

The grey and brown powder samples of K_3IrCl_6 and K_2IrCl_6 , respectively were purchased from Sigma-Aldrich and used without further purification. The Cs_2CuCl_4 orange reference sample was prepared according to published procedures.⁷ The samples were ground and pasted onto an absorber free 0.5 μm thick Kapton tape for transmission and fluorescence, and for carbon tape for electron-yield measurements. The samples on Kapton tape were diluted with boron nitride and pasted as thin as possible to avoid self-absorption, while for the electron-yield measurements samples were applied liberally on carbon tape.

All reported measurements were carried out at beamline 9A of KEK Photon Factory, Tsukuba, Japan set up in SX configuration under ring current of 450 mA in top-off mode. The settings of upstream beamline optics were used as provided by the staff scientists. The beam path, the ionization chamber measuring incident beam intensity, I_0 , and the sample chamber were purged with He. In addition to the reported total fluorescence collected by a 3-element, N_2 purged Lytle detector, we have collected data in electron yield, transmission, energy resolved multi-element solid state detector with soller slits as well that will allow us to develop the detector dependence of the transition dipole integral in Eq.(1). We wish to highlight that PF BL9A provides an optimized experimental set up for simultaneous collection of all the above signals that is unique among synchrotron facilities worldwide.

The angle positions of the monochromator crystals were calibrated to the pre-edge energy position of Cs_2CuCl_4 reference compounds to be at 2820.2 eV. In order to be consistent with previous Cl K-XANES measurements we have used the region file as shown in Table 1 instead of using the standard XANES or EXAFS scan regions. For all samples, at least three scans were collected and averaged. No radiation damage has been observed even without using the liquid He-free cryostage.

Table 1: Definition of the Cl K-XANES ‘fine’ scan (single sweep takes 15.5 min with 1 sec integration time)

energy range, eV	stepsize, eV	steps
2770-2810	2.0	20
2810-2850	0.1	400
2850-2910	0.5	120
2910-3080	5.0	35

Data reduction and normalization were carried out by the Automated Data Reduction Program developed by D. Gardenghi.¹² Fitting of pre-edge, rising-edge, and edge jump features was achieved by using PeakFit v4.12 (SeaSolve). The spectral features and the edge jump were fitted with pseudo-Voigt line shape and an arctangent function, respectively.

Electronic structure calculations were carried out using Amsterdam Density Functional package¹³ using BP86^{14,15} (pure GGA), B3LYP^{16,17} and BHLYP^{17,18} (hybrid GGA), M06-L¹⁹ (meta-GGA), M06-HF²⁰ (hybrid meta-GGA) functionals with all-electron triple- ζ quality basis set supplemented with double polarization functions for all atoms (denoted as TZV2P).²¹ Relativistic scalar zeroth order regular approximation (ZORA²²) formalism and empirical dispersion correction by Grimme²³ were also applied. The Ir(IV) complex has an $S=1/2$ ground state, which required the use of spin unrestricted DFT calculations.

3 Results and Discussion

Figure 1 presents the two reference spectra generally used for the quantitative analysis of Cl K-edge. The free chloride ligand salt spectrum as in NaCl shows a

featureless rising-edge that is superimposed to the Cl $1s \rightarrow$ continuum ionization edge jump. The rising-edge arises from the Cl $1s \rightarrow 4p$ localized, bound state excitation. The Cl $4p$ orbitals can be considered as Rydberg-type orbitals, since they do not contribute to chemical bonding to an appreciable degree. Therefore, it is common to use the first inflection point along the rising-edge as the measure of the absorber’s effective nuclear charge seen by the core $1s$ electron. This is a direct measure of the charge on the ligand and thus it can be correlated with the ionic character of a M-L bond.

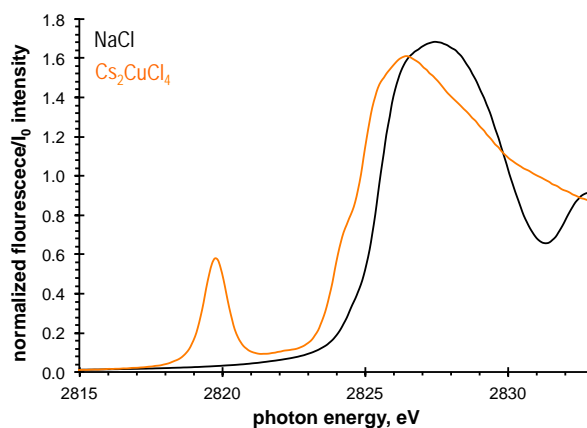


Fig. 1: Reference Cl K-XANES for free chloride ligand salt NaCl (black) and Cs_2CuCl_4 complex (orange)

In going from the NaCl salt to the Cs_2CuCl_4 complex, an electron hole is opening up in the Cu $3d$ manifold due to the $3d^9$ electron configuration and a new spectral feature is observed at lower energy than the edge jump, called pre-edge feature. As described in literature,⁷ the intensity of this feature is directly proportional to the covalency of the Cu-Cl bond as represented by Eq.(1). From an extensive set of spectroscopic data,¹⁰ the integrated pre-edge intensity of 0.73 eV measured at KEK PF BL9A using Lytle fluorescence detector corresponds to $30 \pm 4\%$.

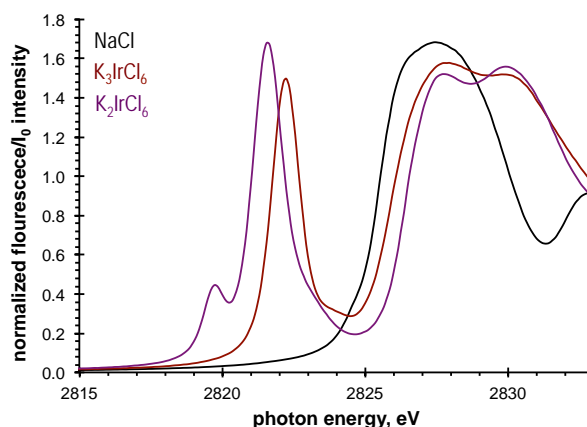


Fig. 2: Comparison of Cl K-XANES spectra of $Ir^{(III)}$ (brown) and $Ir^{(IV)}$ (purple) chloride complexes, and the free ligand (NaCl) salt

The comparison of the spectral features in Figure 2, clearly shows the remarkable changes in the chloride ligands upon coordination to the Ir^(III) and Ir^(IV) ions with 5d⁶ and 5d⁵ electron configurations, respectively. The rising-edge shifts to higher up in energy in Ir^(III) and then even more in Ir^(IV) complex relative to NaCl as a result of an increasing amount of Cl→Ir electron donation as the number of electron holes increases and thus the chloride ligand becomes less nucleophilic. An even more remarkable spectral feature is the intensity of the pre-edge feature(s). The K₃IrCl₆ complex has a single pre-edge peak that corresponds to the Cl 1s→e_g^{*} excitation. The presence of a single spectral feature is the experimental evidence for the diamagnetic state of the Ir^(III) centre with t_{2g}⁶ electron configuration. Upon oxidation an electron hole is opened in the t_{2g} set of orbitals and this unambiguously shows up in the spectra as a new pre-edge feature at 2819.6 eV. The energy gap between the lower and higher energy pre-edge features is the direct experimental measure of ligand field splitting (10Dq) in the K₂IrCl₆ complex (1.9 eV). In addition, the oxidation increases the effective nuclear charge of the Ir centre and thus the 5d manifold gets stabilized and hence the shift of the pre-edge features to lower energy than that of the K₃IrCl₆ complex. The actual 5d manifold energy shift is even greater (1.1 eV) than the energy difference between the two intense pre-edge features corresponding to the e_g^{*} orbitals (-0.6 eV), since the Cl K-edge edge jump shifts up by +0.5 eV in going from K₃IrCl₆ to K₂IrCl₆ complex.

In order to extract Ir-Cl bond covalency information, we need to consider the number of absorbers in the four compounds we have studied. The renormalized Cl K-XANES spectra are shown in Figure 3, which now allows for the direct comparison of the pre-edge intensities and thus obtaining experimental measures of Ir-Cl bond covalency on the basis of known Cu-Cl bond covalency.

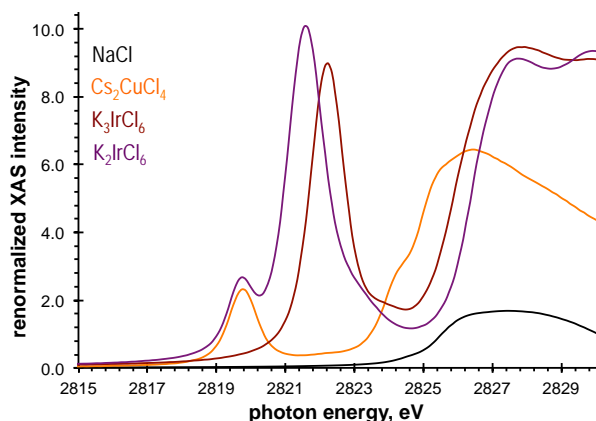


Fig. 3: Renormalized Cl K-XANES spectra of Ir^(III) (brown) and Ir^(IV) (purple) chloride complexes with six absorbers (N=6), and the reference Cs₂CuCl₄ (orange) complex with four absorber (N=4) and free ligand (NaCl) salt with a single Cl absorber

Table 2 summarizes the fitting parameters used to obtain the normalized, integrated pre-edge intensities. Using Eq.(1) and considering the number of holes ($h = 1$,

4, and 4+1) for Cs₂CuCl₄, K₃IrCl₆, and K₂IrCl₆, respectively, and the renormalized intensities from Figure 3, we can determine the Ir-Cl bond covalency for the σ -bonding involving the e_g^{*} orbitals to be 36±2% and 41±2% for the Ir^(III) and Ir^(IV) chloride complexes, respectively. The slightly increased Ir-Cl bond covalency for the latter is the result of better donation to a more oxidized metal centre than in the former. Generally, the M-L π bonding is considered to be less covalent due to the non-ideal orbital overlap than corresponding σ bonding, which is confirmed by our measurements since the new electron hole in Ir^(IV) relative to Ir^(III) has about 30±2% Cl 3p character.

Table 2: Summary of fitting parameters to the pre-edge features of the Cl K-XANES spectra

Complex	E _i ^a , eV	A ^b	hhfw, ^c eV	D ₀
Cs ₂ CuCl ₆	2819.7	0.55	1.06	0.73
K ₃ IrCl ₆	2822.1	1.47	1.26	2.34
K ₂ IrCl ₆	2819.6	0.34	1.10	0.48
	2821.5	1.62	1.30	2.69

^a peak position, ^b amplitude, ^c half height full width

The graphical illustrations of the orbitals experimentally probed are shown in Figure 4. Cursory inspection of the orbital contour plots would indicate a greater chloride contribution (60-70%) to these frontier unoccupied molecular orbitals than seen experimentally (30-40%). This indicates that the theoretically calculated electron density distribution per molecular orbital corresponds to an overly covalent electronic structure description. It is also important to mention that due to Jahn-Teller distortion in the hexacoordinate, low spin Ir^(IV) complex, the effective symmetry of the [IrCl₆]²⁻ complex was D_{3d}, with a trigonally distorted octahedral coordination environment.

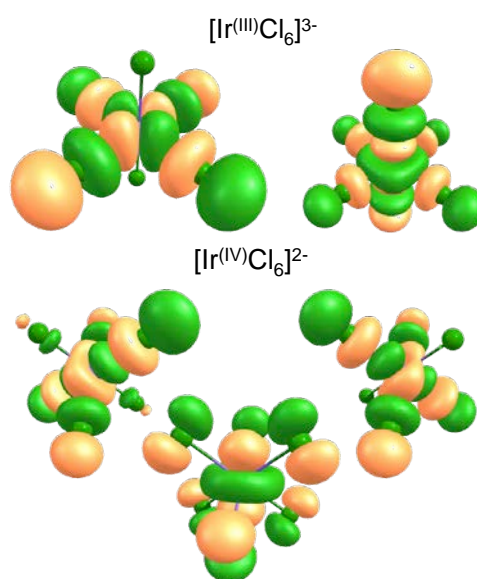


Fig. 4: Acceptor molecular orbitals probed by Cl K-XANES spectroscopy resulting in the appearance of intense pre-edge features

Table 3: DFT-based calculated composition of the e_g^* orbital in the $O_h [Ir^{(III)}Cl_6]^{2-}$ complex (for all calculations the TZV2P basis set was used)

DFT method		dispersion correction	relativistic correction	Ir 5d	Cl 3s	Cl 3p	Cl 3d
pure GGA	BP86			49%	1%	48%	2%
	BP86		scalar ZORA	53%	1%	44%	2%
hybrid GGA	B3LYP			52%	1%	45%	2%
	B3LYP	Grimme3		52%	1%	45%	2%
	B3LYP		scalar ZORA	56%	1%	41%	2%
	B3LYP	Grimme3	scalar ZORA	55%	2%	41%	2%
	BHHLYP			63%	0%	35%	2%
metaGGA	BHHLYP		scalar ZORA	66%	1%	31%	2%
	M06-L			56%	0%	42%	2%
hybrid metaGGA	M06-L		scalar ZORA	59%	1%	38%	3%
	M06-HF			43%	3%	52%	2%
	M06-HF		scalar ZORA	46%	5%	47%	2%

Experimental Cl 3p character from the Cl K-XANES pre-edge intensities is $36 \pm 2\%$.

Since we have a direct way of experimentally determining the composition of the antibonding M-L orbitals, we can use this approach to evaluate the performance of density functionals at the level of the electronic structure, orbital compositions in terms of absolute values, which is often rare in theoretical chemistry. Table 3 presents a representative list of density functional theory results for the $O_h [Ir^{(III)}Cl_6]^{2-}$ complex calculated in its experimental crystal structure.

As graphically illustrated by Figure 4, the pure GGA functionals can provide an overly covalent picture. While the popular hybrid GGA functional of B3LYP improves the ground state electronic structure description it is still considerably off from the experimental value. It is important to emphasize that the dispersion correction only affect the electronic structure to a negligible degree; however, the consideration of relativistic effects gives a more ionic electronic structure by about 4-5%. The empirical adjustment of the amount of HF exchange mixed with the density functional exchange up to 50% improves the ground state electronic structure to the vicinity of the experimental value. It is notable that a hybrid GGA functional (Becke's half and half) that works reasonably well for the Ir complexes also gave a good agreement for the Pd complexes⁶ in an earlier study. From Table 3, the best agreement between the calculated and the experimental Cl 3p character without empirical adjustment was achieved by using Truhlar's M06-L functional. This is the recommended functional to be used for computational structure/function studies of Ir complexes.

In conclusion, we used the world-class facilities of KEK-PF beamline 9A to enter into the world of iridium complexes through ligand K-edge X-ray absorption spectroscopic measurements. We have experimentally defined the ground state electronic structure of two prototypical Ir complexes with oxidation states of III and

IV. From the pre-edge intensities at the Cl K-edge, we determined the covalency of the Ir-Cl bond. This information from complementarity gives the experimental Ir character of the experimentally probed orbitals that can be measured at the Ir L_3 - and L_2 -edges. Thus, the Cl $1s \rightarrow 3p$ transition dipole integral can be used to obtain a reasonable estimate for the Ir $2p \rightarrow 5d$ excitations. This can be used to propagate both integrals to other edges such as P and S K-edges from the tender X-ray range, C and O K-edges from the soft X-ray range, and Br and I K-edges from the hard X-ray energy range. Furthermore, the experimental definition of the Ir-Cl bond allowed for the evaluation of representative density functional theory calculations with respect of orbital compositions. We have found that the BHHLYP hybrid GGA or the M06-L metaGGA functionals provide the most reasonable electronic structure description of the studied iridium complexes.

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Research Achievements

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* szilagyi@montana.edu