

# Supporting Information:

## Valence-to-Core X-Ray Emission Spectroscopy of Transition Metal Tetrahalides: Mechanisms Governing Intensity

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## A Input files, xyz files and XES Raw Data

All input files as well as coordinate (.xyz) files, xes raw data and data needed for reproduction of figures within the manuscript can be found online: <https://doi.org/10.17617/3.JECRGR>

## B $[\text{MX}_4]^{2-}$ Mainline Tail Fits

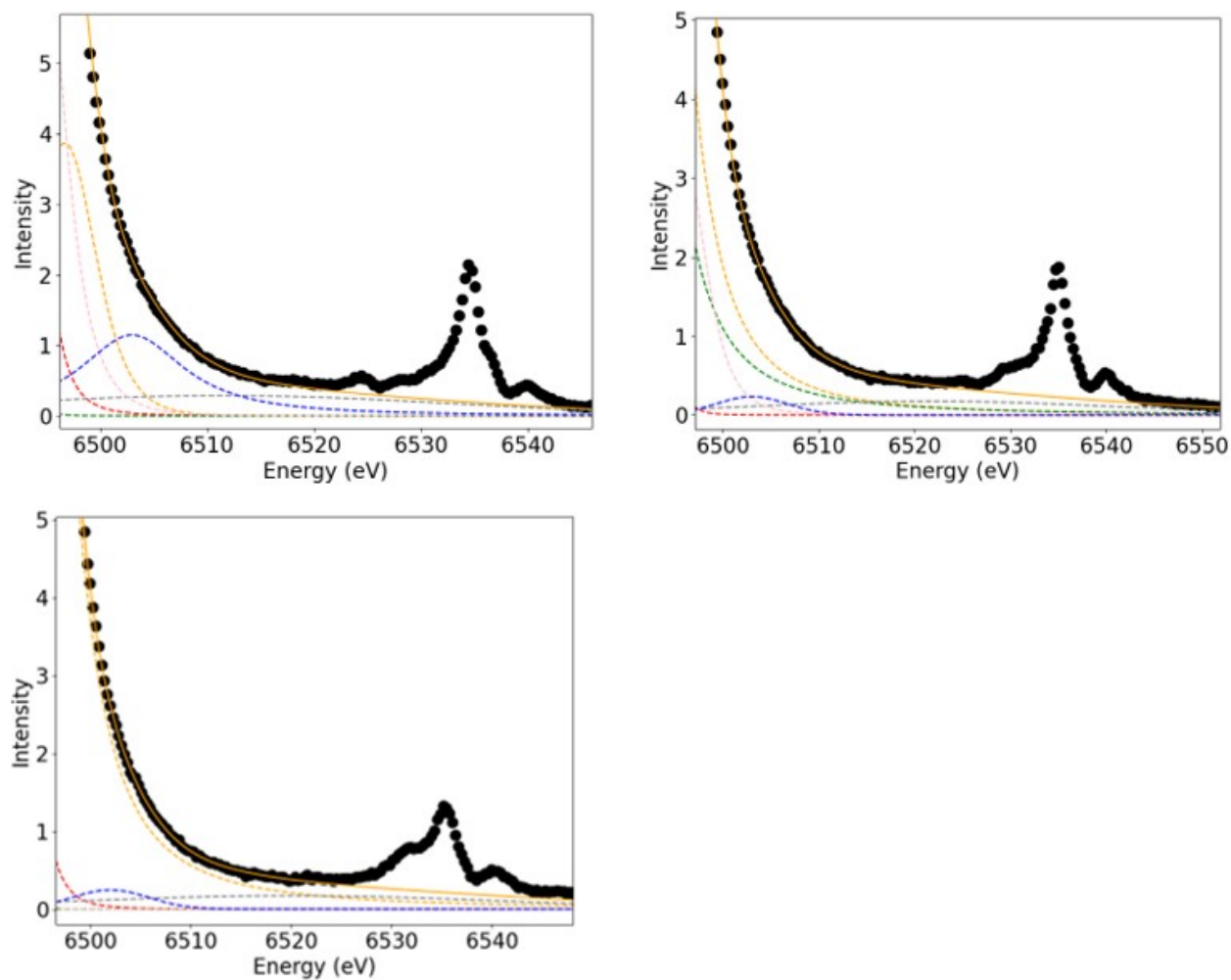


Figure S1. Mainline tail fits of the manganese halide series (top left:  $[\text{MnCl}_4]^{2-}$ , top right:  $[\text{MnBr}_4]^{2-}$ , bottom:  $[\text{MnI}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

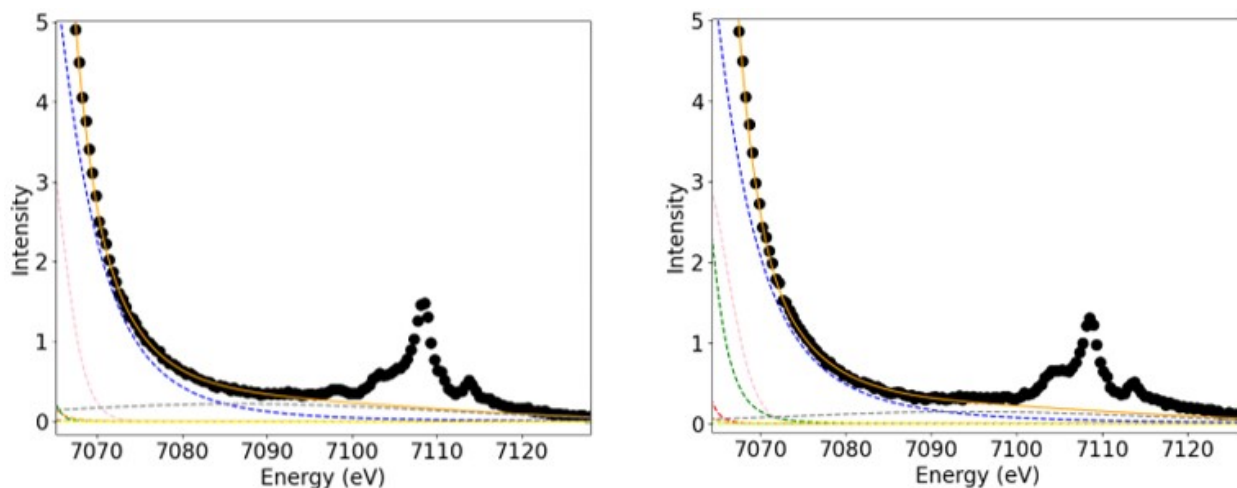


Figure S2. Mainline tail fits of the iron halide series (left:  $[\text{FeCl}_4]^{2-}$ , right:  $[\text{FeBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

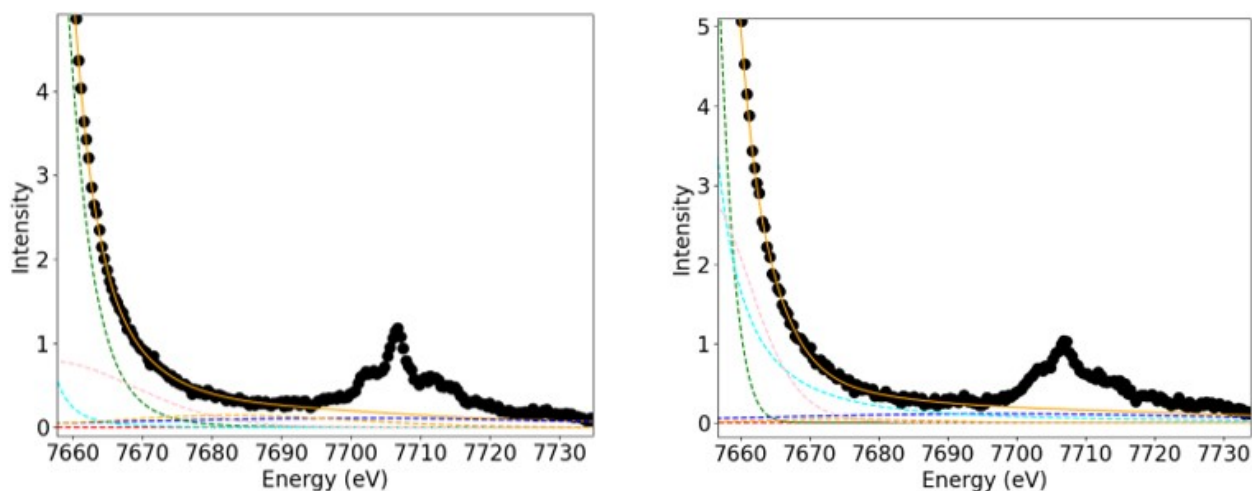


Figure S3. Mainline tail fits of the cobalt halide series (left:  $[\text{CoCl}_4]^{2-}$ , right:  $[\text{CoBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

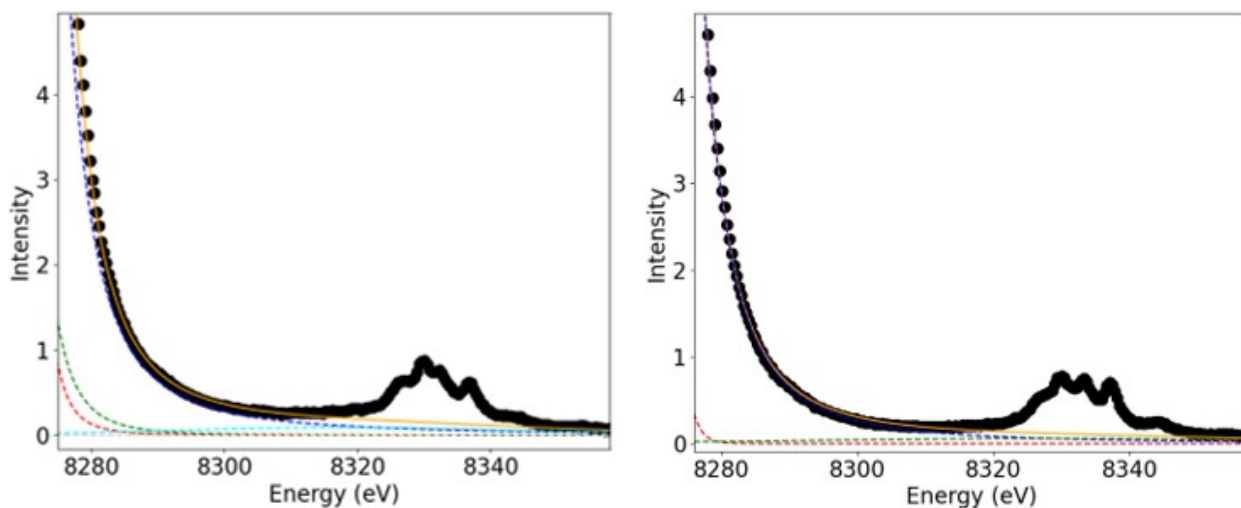


Figure S4. Mainline tail fits of the nickel halide series (left:  $[\text{NiCl}_4]^{2-}$ , right:  $[\text{NiBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

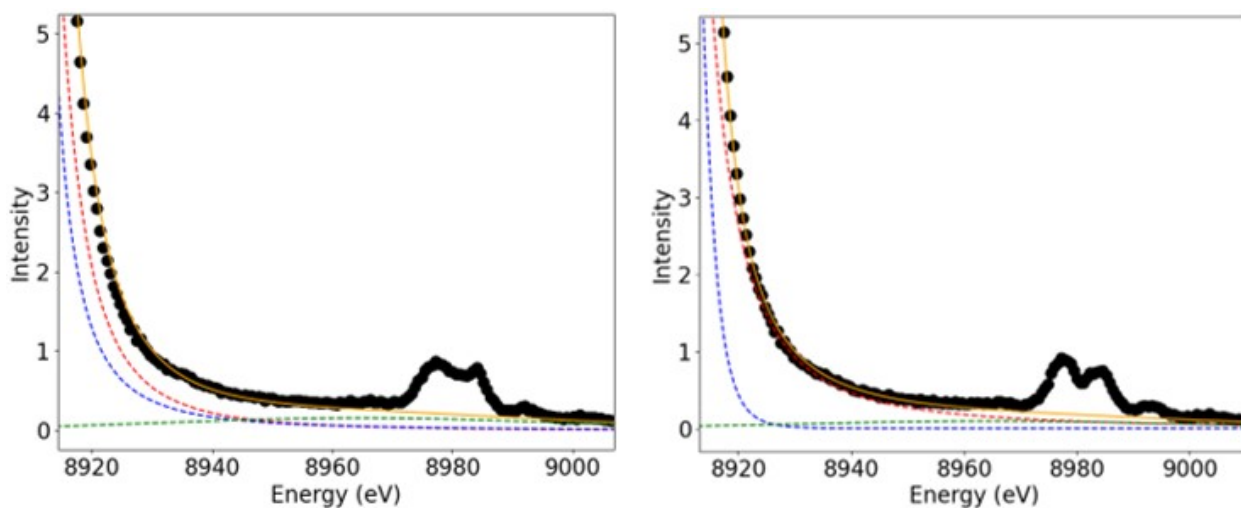


Figure S5. Mainline tail fits of the copper halide series (left:  $[\text{CuCl}_4]^{2-}$ , right:  $[\text{CuBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

### C VtC fits

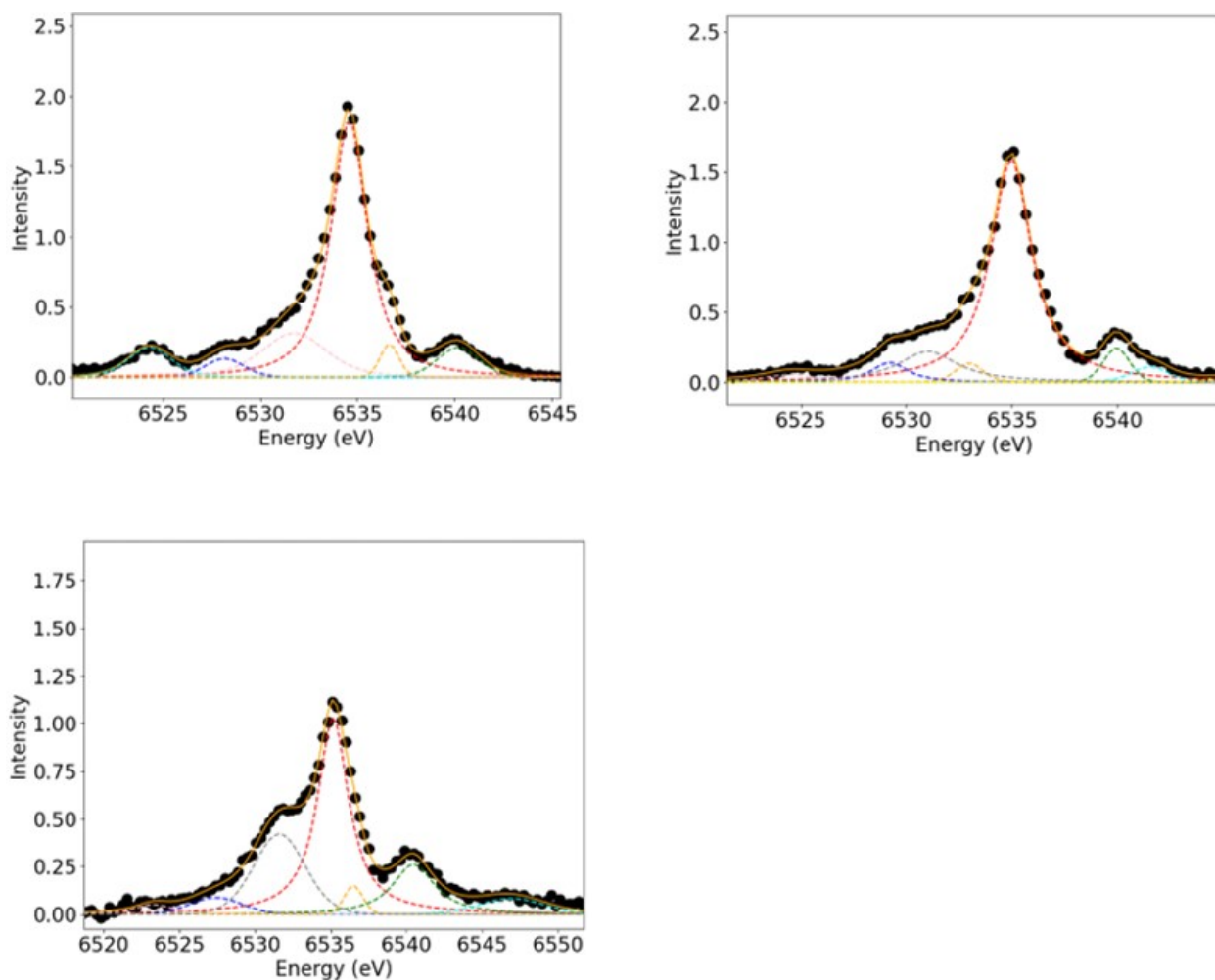


Figure S6. VtC fits of the manganese halide series (top left:  $[\text{MnCl}_4]^{2-}$ , top right:  $[\text{MnBr}_4]^{2-}$ , bottom:  $[\text{MnI}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

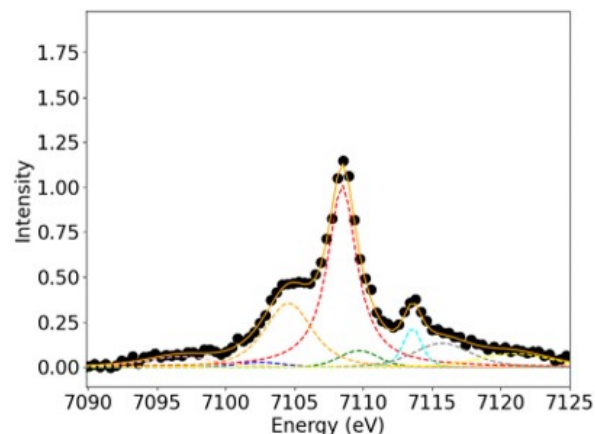
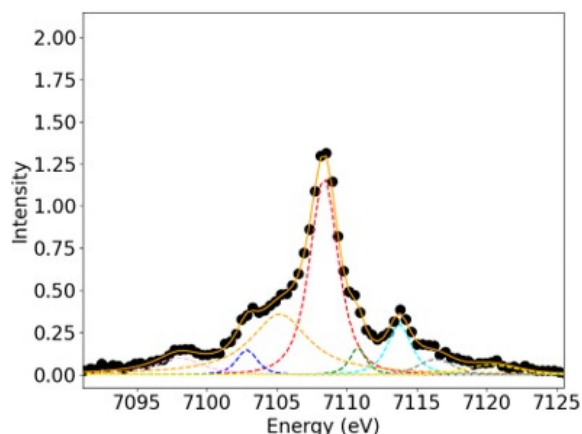


Figure S7. VtC fits of the iron halide series (left:  $[\text{FeCl}_4]^{2-}$ , right:  $[\text{FeBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

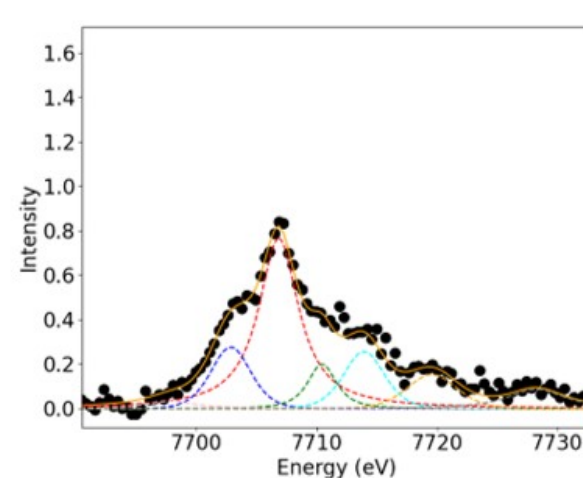
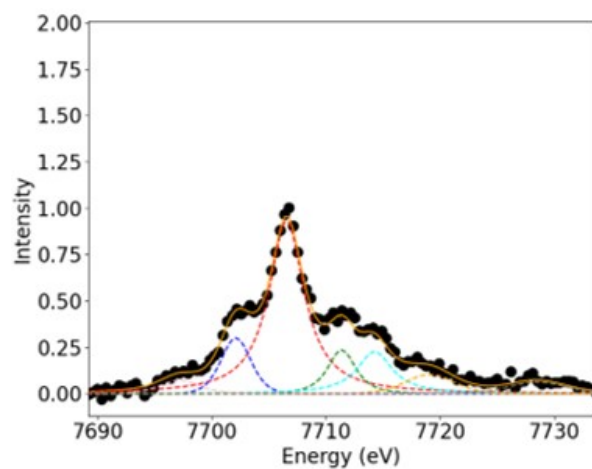


Figure S8. VtC fits of the cobalt halide series (left:  $[\text{CoCl}_4]^{2-}$ , right:  $[\text{CoBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

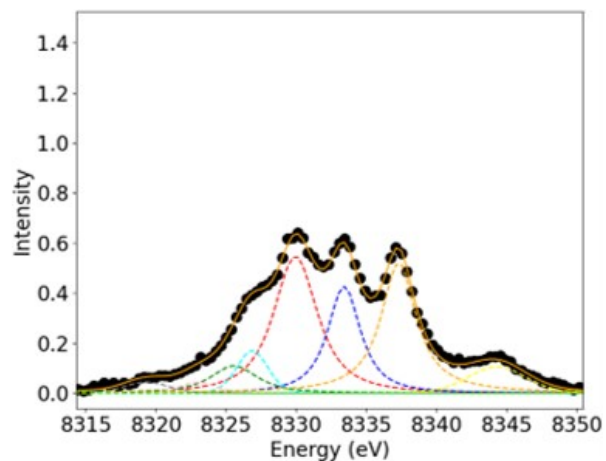
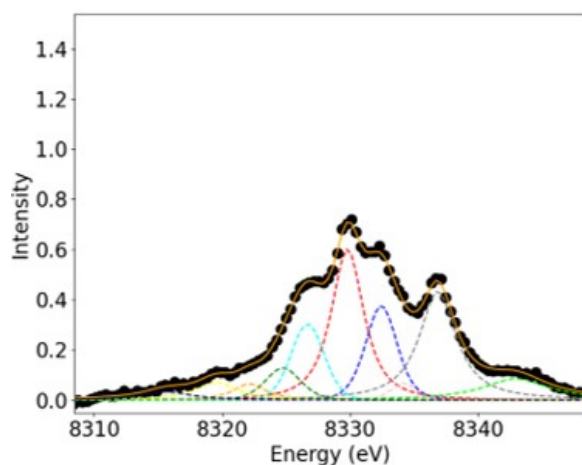


Figure S9. VtC fits of the nickel halide series (left:  $[\text{NiCl}_4]^{2-}$ , right:  $[\text{NiBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

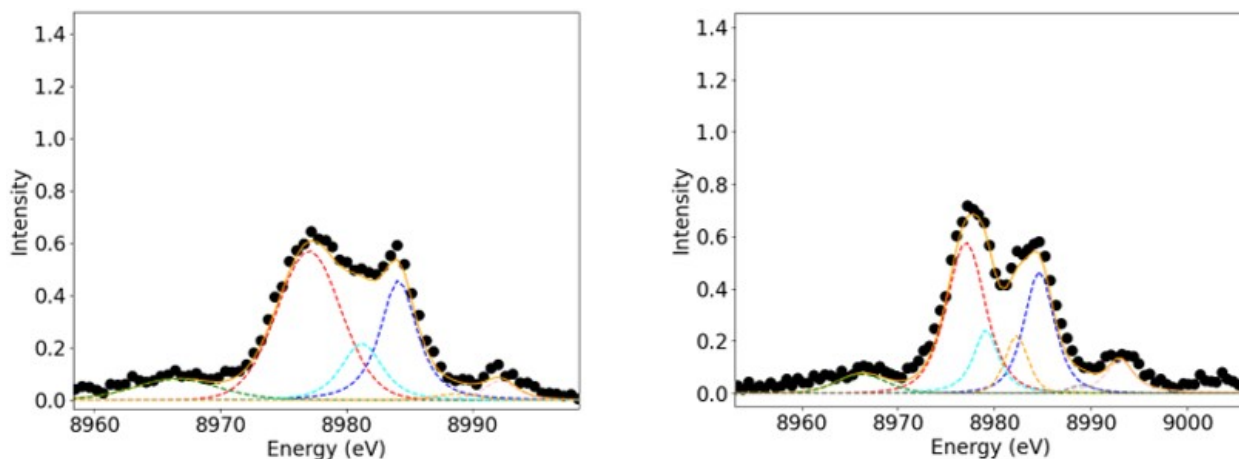


Figure S10. VtC fits of the copper halide series (left:  $[\text{CuCl}_4]^{2-}$ , right:  $[\text{CuBr}_4]^{2-}$ ). Experimental data are shown in black. The fit components are shown with colored dashed lines and the total fit is given by the solid orange line.

#### D Correlation of p Contribution vs. Oscillator Strength For Loewdin Population Analysis (left) Compared to LCAO Analysis (right) For The Exemplary $[\text{MnCl}_4]^{2-}$ Molecule

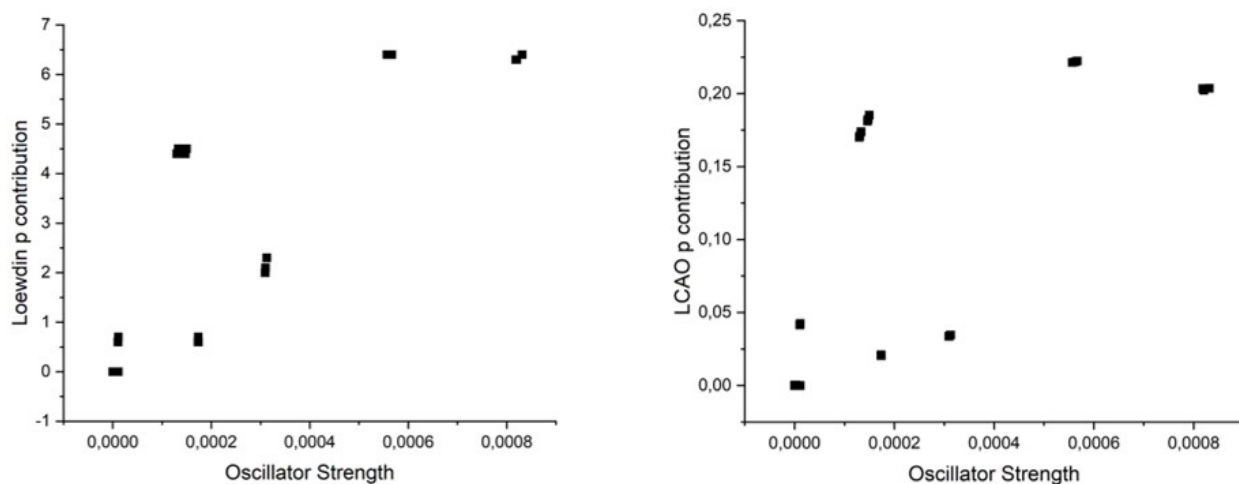


Figure S11. Loewdin p contribution (left) and LCAO p contribution (right) vs. oscillator strength for the exemplary  $[\text{MnCl}_4]^{2-}$  molecule.

## E Comparison of the LCAO 3p and 4p Contribution For The Exemplary $[\text{MnCl}_4]^{2-}$ Molecule

Peak region	MO's contributing to VtC intensity	Mn 3p contribution to MO	Mn 4p contribution to MO
$\text{K}\beta''$	30 $\alpha$	$1.6 \cdot 10^{-5}$	0,174
	31 $\alpha$	$1.6 \cdot 10^{-5}$	0,171
	32 $\alpha$	$1.6 \cdot 10^{-5}$	0,17
	30 $\beta$	$3.8 \cdot 10^{-5}$	0,185
	31 $\beta$	$3.8 \cdot 10^{-5}$	0,182
	32 $\beta$	$3.7 \cdot 10^{-5}$	0,181
$\text{K}\beta_{2,5}$	33 $\alpha$	$1.1 \cdot 10^{-5}$	0,02
	34 $\alpha$	$1.1 \cdot 10^{-5}$	0,021
	35 $\alpha$	$1.1 \cdot 10^{-5}$	0,021
	34 $\beta$	$4.0 \cdot 10^{-5}$	0,204
	35 $\beta$	$3.9 \cdot 10^{-5}$	0,202
	36 $\beta$	$3.9 \cdot 10^{-5}$	0,203
	39 $\alpha$	$9.8 \cdot 10^{-6}$	0,222
	40 $\alpha$	$9.7 \cdot 10^{-6}$	0,222
	41 $\alpha$	$9.6 \cdot 10^{-6}$	0,221
	39 $\beta$	$1.2 \cdot 10^{-8}$	0,041
	40 $\beta$	$1.5 \cdot 10^{-8}$	0,042
	41 $\beta$	$1.7 \cdot 10^{-8}$	0,042
	47 $\alpha$	$3.4 \cdot 10^{-6}$	0,034
	48 $\alpha$	$3.4 \cdot 10^{-6}$	0,034
49 $\alpha$	$3.4 \cdot 10^{-6}$	0,035	

## F Definition of the Transition Dipole Moment And Relation to Oscillator Strength

According to Fermi's golden rule, the intensity of an electronic transition from initial state  $|\psi_I\rangle$  to final state  $|\psi_F\rangle$  is proportional to the square of corresponding transition dipole moment, i.e.

$$I_{IF} \propto |\langle \psi_I | \hat{\vec{\mu}} | \psi_F \rangle|^2 \quad (1)$$

The dipole operator has incorporated positions and charges from all nuclei and electrons:

$$\hat{\vec{\mu}} = \sum_A Q_A \vec{R}_A - \sum_i \vec{r}_i \quad (2)$$

As all positions  $\vec{R}_A$  and  $\vec{r}_i$  are vectors in position space with 3 components each,  $\hat{\vec{\mu}}$  is a vectorial quantity, too. The three components

$$T_{IF}^x = \langle \langle \psi_I | \hat{\mu}_x | \psi_F \rangle \rangle \quad (3)$$

$$T_{IF}^y = \langle \langle \psi_I | \hat{\mu}_y | \psi_F \rangle \rangle \quad (4)$$

$$T_{IF}^z = \langle \langle \psi_I | \hat{\mu}_z | \psi_F \rangle \rangle \quad (5)$$

are the transition dipole moments along the  $x$ ,  $y$  and  $z$  axes, respectively. However, the right hand side of equation (1) incorporates the square of  $\vec{\mu}$  which is the sum of the square of all three vector components, i.e.

$$I_{IF} \propto |T_{IF}^x|^2 + |T_{IF}^y|^2 + |T_{IF}^z|^2 \quad (6)$$

In case of transition metal K-edge VtC spectroscopy, the initial state corresponds to a core excited ionized state with a hole in the  $1s$  shell of the transition metal while in the final state said core hole is filled by a valence electron. When two-electron processes and correlation effects that would lead to the involvement of higher excited configurations are neglected,  $\psi_F$  and  $\psi_I$  consist of a single electronic configuration. In that case, the transition dipole moment between the two states reduces to a transition dipole moment between the two orbitals involved in aforementioned electronic transition:

$$|\langle \psi_I | \vec{\mu} | \psi_F \rangle| \approx |\langle \Phi_p | \vec{\mu} | 1s \rangle| \quad (7)$$

Here  $|\Phi_p\rangle$  denotes the valence orbital involved in the VtC transition and  $|1s\rangle$  is the transition metal  $1s$  orbital.

The transition dipole moment  $\mu_i$  of a transition is related to the oscillator strength  $f$  of the transition via

$$f = \frac{2m_e \Delta E}{3\hbar^2 e^2} |\mu_i|^2 \quad (8)$$

where  $m_e$  is the mass of the electron,  $\Delta E$  is the energy of the transition,  $\hbar$  is the reduced Planck constant and  $e$  is the charge of the electron.