Supplementary Information:

Origin of dark-channel X-ray fluorescence from transition-metal ions in water

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Theoretical Modelling:

To quantify the charge transfer and its direction from X-ray absorption spectra we use ligand field multiplet (LFM) theory[1,2] and optimized our simulated spectra to the transmission spectra at the L-edge of Co2+ in H_2O. This approach takes into account all the electronic Coulomb interactions as well as spin-orbit coupling for every shell and local geometrical environment of the absorbing atom applied through the crystal field potential.[3] The spectrum is calculated from the sum of all possible transitions for an electron excited from the 2p level into a 3d level. Dipole allowed 2p→4s transition is neglected due to its low probability. To take into account ligand-to-metal and metal-to-ligand charge transfer (LMCT and MLCT) introduced by covalence, the ground state of a $3d^7$ Co ion is taken to be a linear combination of three configurations, $3d^6L^-$, $3d^7$, and $3d^8\underline{L}$.[4,5] Co coordination number considered to be six from shape of transmission spectra.[3] Therefore octahedral surrounding of the Co ion is represented by an O_h crystal field parameter, which strength is given by the crystal field parameter 10Dq. In order to consider lifetime and instrumental broadening calculated transitions were Lorentzian broadened with an fwhm of 0.2 eV over the L_3 edge and 0.35 eV over the L_2 edge and with a Gaussian fwhm of 0.2 eV respectively. Further optimized parameters are given in table S.1. Insignificant values of charge transfer used in multiplet simulations which give the best agreement to experimental data suggest weak covalence of Co-O(H_2O) bonds. The Slater-Condon-Shortly parameters were reduced to 80% of their Hartree-Fock calculated values. This reduction factor value does not include additional nephelauxetic effect which is also support weak covalence of Co-O(H2O) bond.

Table S.1

Ground state configuration considered to reproduce the experimental X-ray absobtion associated to $CoCl_2$ dissolved in water and D_2O. Here L^- denotes MLCT.

	CoCl$_2$ in H$_2$O
Ground state configuration	1.3 % d^6L^-
	82.9 % d^7
	15.8 % $d^8\underline{L}$
Reduction factor κ (%)	80
E_a (eV)	782.1
ξ_{2p} (eV)	9.75
ξ_{3d} (eV)	0.02
10Dq (eV)	1.1
ΔLM (eV)	3.5
ΔML (eV)	10.0
U-Q (eV)	-1.0
$d^6 L^-$ T(e_g)	0.0
$d^6 L^-$ T(t_{2g})	1.0
$d^8 \underline{L}$ T(e_g)	3.8
$d^8 \underline{L}$ T(t_{2g})	3.8

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