Supporting Information: Determination of Contact Ion-Pair Formation in $CoCl_2$ Aqueous, Methanol, and Ethanol Dilute Solutions by UV-vis and X-ray Absorption Spectroscopies

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1 Supplementary Figures (Figures S1-S5)

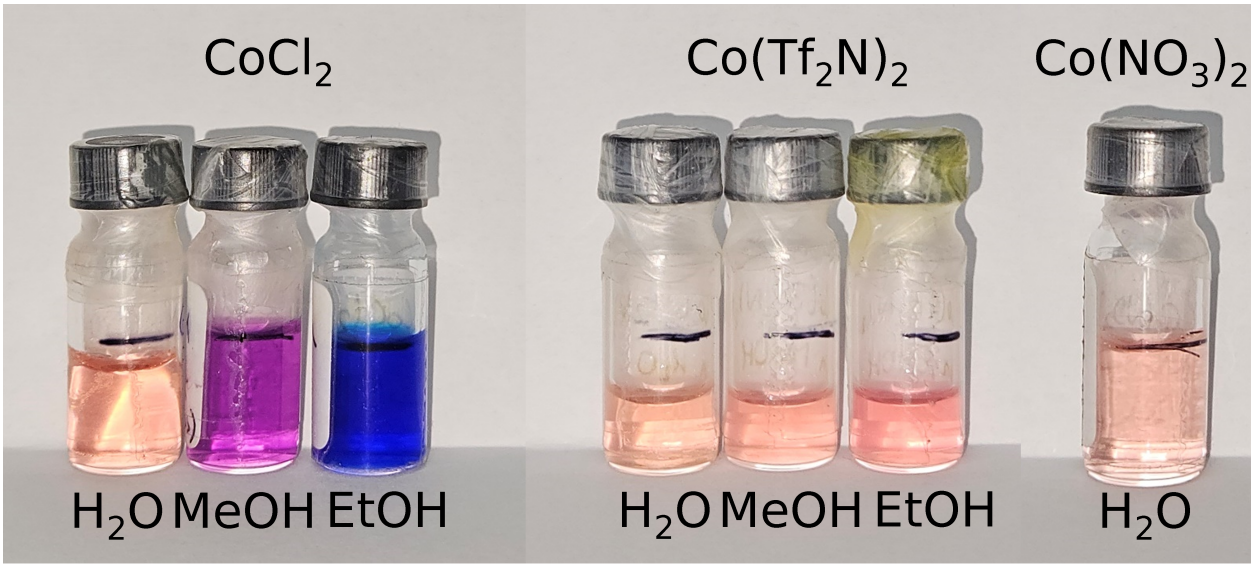

Figure S1: Photographs of the 0.1 mol L^{-1} $CoCl_2$, $Co(Tf_2N)_2$ ($Tf_2N = (CF_3SO_2)_2N^-$), and $Co(NO_3)_2$ aqueous, methanol (MeOH), and ethanol (EtOH) solutions investigated in this work.

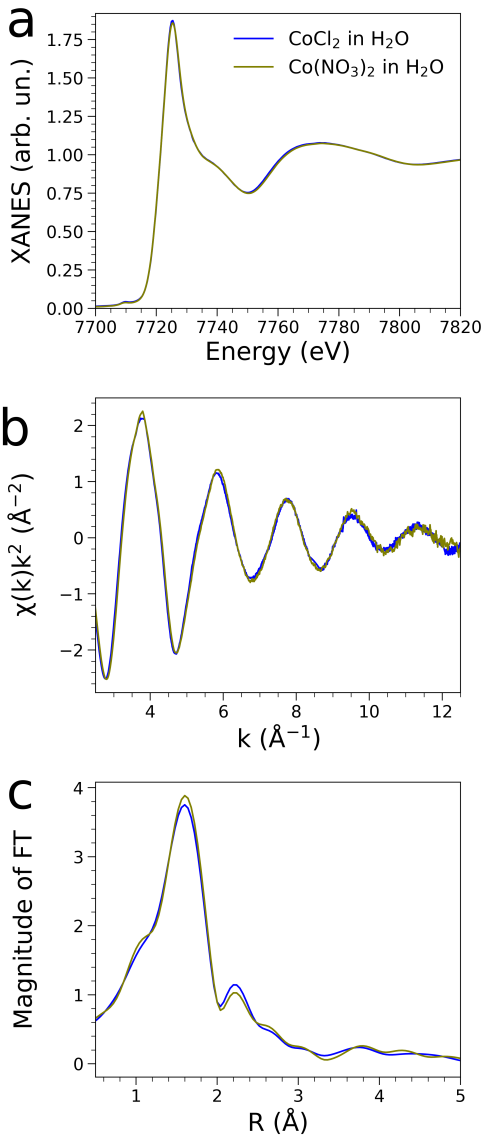

Figure S2: Co K-edge a) normalized X-ray absorption near edge structure (XANES), b) extended X-ray absorption fine structure (EXAFS), and b) non-phase shift-corrected Fourier Transform (FT) experimental spectra collected on the 0.1 mol L^{-1} $CoCl_2$ and $Co(NO_3)_2$ aqueous solutions. The FT's have been calculated in the 2.3 - 12.0 $Å^{-1}$ k-range.

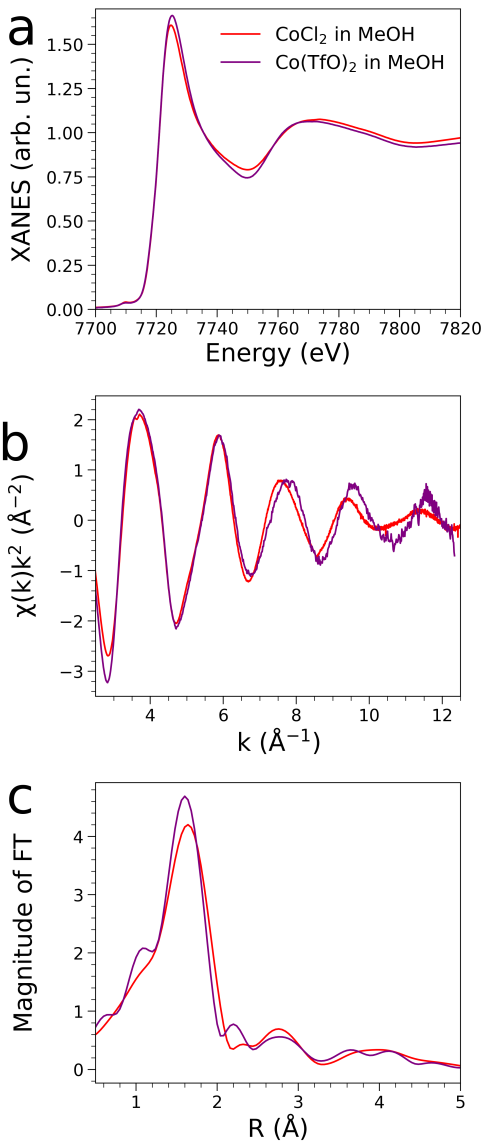

Figure S3: Co K-edge a) normalized XANES, b) EXAFS, and b) non-phase shift-corrected FT experimental spectra collected on the 0.1 mol L^{-1} $CoCl_2$ and $Co(TfO)_2$ ($TfO = CF_3SO_3^-$) solutions in MeOH. The FT's have been calculated in the 2.3 - 12.0 $Å^{-1}$ k-range.

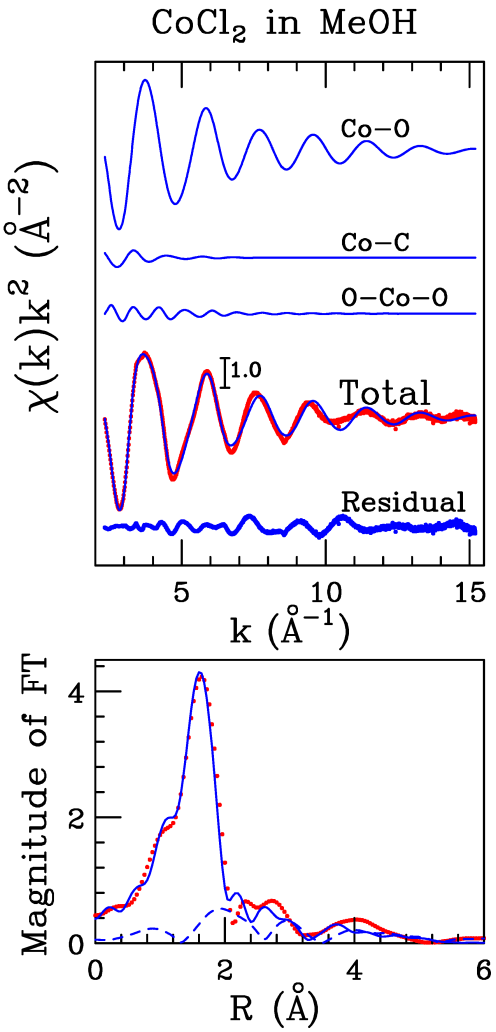

Figure S4: Analysis of the Co K-edge EXAFS spectrum collected on the 0.1 mol L^{-1} $CoCl_2$ solution in MeOH carried out assuming six-fold MeOH coordination. Upper panel: best-fit single-scattering (SS) and multiple-scattering (MS) theoretical signals, together with the total theoretical contribution (blue lines) compared with the experimental data (red dots) and the resulting residuals (blue dots). Lower panel: non-phase shift-corrected FT's of the best-fit theoretical signal (blue line), of the experimental data (red dots), and of the residuals (blue fragmented line).

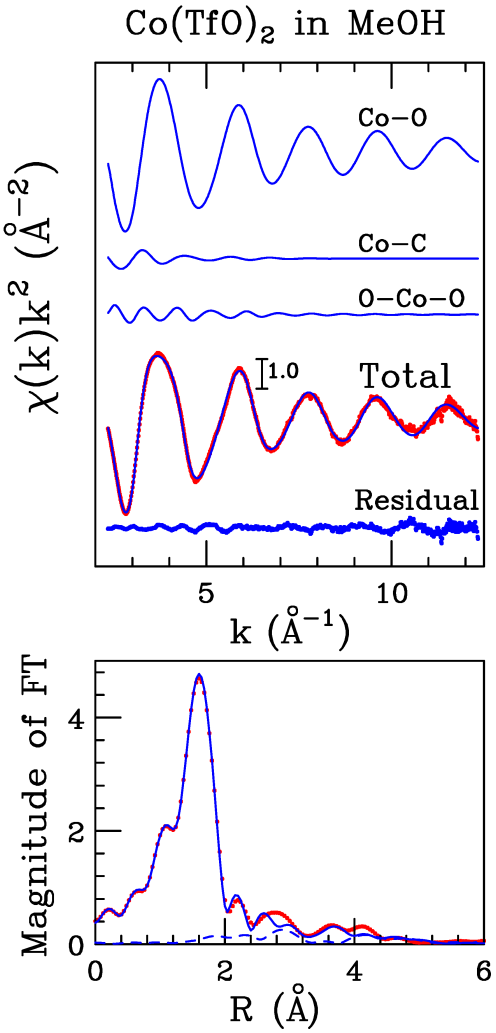

Figure S5: Analysis of the Co K-edge EXAFS spectrum collected on the 0.1 mol L^{-1} $Co(TfO)_2$ solution in MeOH. Upper panel: best-fit SS and MS theoretical signals, together with the total theoretical contribution (blue lines) compared with the experimental data (red dots) and the resulting residuals (blue dots). Lower panel: non-phase shift-corrected FT's of the best-fit theoretical signal (blue line), of the experimental data (red dots), and of the residuals (blue fragmented line).

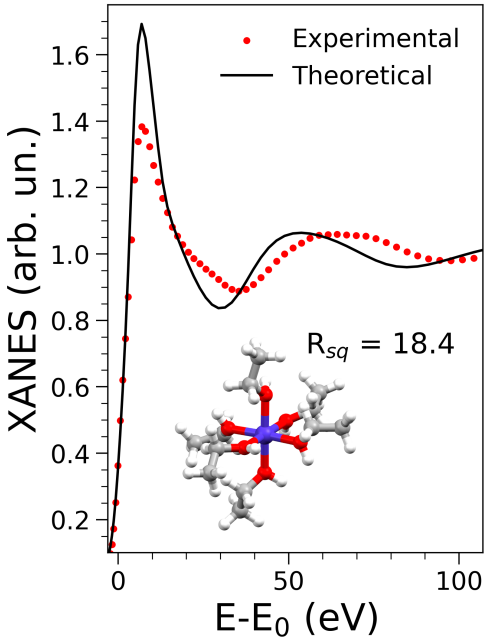

Figure S6: Experimental Co K-edge XANES spectrum of the 0.1 mol L^{-1} $CoCl_2$ solution in EtOH (red dots) compared with the MXAN best-fit calculations for the $[Co(EtOH)_6]^{2+}$ cluster (black full line). The residual function R_{sq} is reported together with the optimized cluster (cobalt is purple, oxygen is red, carbon is gray, and hydrogen is white).

2 Supplementary Tables (Tables S1 - S2)

Table S1: List of the prepared 0.1 mol L^{-1} cobalt salt solutions.

Salt	Solvent
$CoCl_2$	Water
$Co(NO_3)_2$	Water
$Co(Tf_2N)_2$	Water
$CoCl_2$	MeOH
$Co(TfO)_2$	MeOH
$Co(Tf_2N)_2$	MeOH
$CoCl_2$	EtOH
$Co(Tf_2N)_2$	EtOH

Table S2: Best-fit structural parameters for the two-body distributions obtained from the EXAFS analysis of the 0.1 mol L^{-1} $Co(TfO)_2$ solution in MeOH. N is the coordination number, R the average distance, σ^2 the Debye-Waller factor, and β the asymmetry index.

		N	R (Å)	σ^2 (Å^{-2})	β
$Co(TfO)_2$ in MeOH	Co-O	6.0(3)	2.09(2)	0.002(2)	0.3(1)
	Co-C	6.0(6)	3.36(5)	0.028(6)	0.0(3)