

**Supporting Information to:**

**Copper(I) speciation in mixed thiosulfate-chloride and ammonia-chloride solutions: XAS & UV-Visible spectroscopic studies**

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Table S1: Compositions of thiosulfate-bearing solution used in XAS measurements.

Sample #	Analytical concentrations (m)			$S_2O_3^{2-}$ / Cu	Stoichio metric ionic strength (m)
	$Cu^+$	Cl <sup>-</sup>	$S_2O_3^{2-}$		
CuS2O3_01F*	0.04626	0.5713	4.81E-02	1.04	0.6206
CuS2O3_02	0.04691	0.5794	9.38E-02	2.00	0.6776
CuS2O3_02D	0.01470	0.1815	2.94E-02	2.00	2.113
CuS2O3_03	0.04727	0.5837	1.42E-01	3.00	0.7356
CuS2O3_03D	0.01475	0.1821	4.42E-02	3.00	0.2273
CuS2O3_05	0.05575	3.9108	1.12E-01	2.00	4.0285
CuS2O3_06	0.05494	3.4571	1.65E-01	3.00	3.6355
CuS2O3_07	0.00211	0.0261	5.28E-03	2.50	0.0314
CuS2O3_08	0.0011	0.0135	1.99E-03	1.82	0.0155
CuS2O3_09	0.00106	0.013	3.17E-03	3.00	0.0162
CuS2O3_10*	0.00317	4.1909	3.68E-03	1.16	4.1896
CuS2O3_11	0.00527	4.1547	8.48E-03	1.61	4.1550
Cu-0.5mLiCl	0.0308	0.5047	-	-	0.4966
Cu-16mLiCl	0.0955	15.955	-	-	15.9299
Cu(II) solution for determination of $SO_2$	$Cu^{2+}$ : 0.0089	0.5494	-	-	0.5441

\*Solutions were filtered though Millipore 0.22  $\mu$ m membranes to remove precipitate. However, post experimental analyses revealed that the sample still contained significant amounts of precipitate in suspension. Thus, these solutions were not considered in the data analysis.

Table S2. Compositions of solutions used for UV-Vis measurements in the Cu(I)-S<sub>2</sub>O<sub>3</sub>-Cl system.

Sample	Cu <sup>+</sup> (m)	Cl <sup>-</sup> (m)	Na <sup>+</sup> (m)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (m)
2a	2.28E-04	2.05	2.05	2.25E-05
2b	1.95E-04	2.00	2.00	5.77E-05
2c	1.95E-04	2.00	2.00	1.38E-04
2d	1.95E-04	2.00	2.00	2.29E-04
2e	1.95E-04	2.00	2.00	3.42E-04
2f	1.95E-04	2.00	2.00	4.58E-04
2g	1.95E-04	2.00	2.01	9.13E-04
2h	2.02E-04	2.01	2.01	1.36E-03
2i	1.95E-04	2.00	2.01	2.16E-03
3a	2.51E-04	3.96	3.96	2.53E-05
3b	2.51E-04	3.96	3.96	7.06E-05
3c	2.52E-04	3.98	3.98	1.26E-04
3d	2.51E-04	3.98	3.98	2.55E-04
3e	2.53E-04	3.98	3.98	3.81E-04
3f	2.51E-04	3.98	3.98	5.15E-04
3g	2.81E-04	3.96	3.96	9.87E-04
3h	2.51E-04	3.96	3.97	1.52E-03
3i	2.51E-04	3.98	3.99	2.53E-03
4a	4.97E-04	4.01	4.01	2.44E-05
4b	4.99E-04	4.01	4.01	7.10E-05
4c	4.97E-04	4.01	4.01	1.29E-04
4d	5.00E-04	4.00	4.00	2.55E-04
4e	4.98E-04	4.00	4.00	3.82E-04
4f	4.97E-04	4.00	4.00	5.15E-04
4g	4.99E-04	4.00	4.00	9.91E-04
4h	4.98E-04	4.00	4.00	1.51E-03
4i	4.97E-04	4.00	4.00	2.53E-03
5a	4.52E-04	0.56	0.56	4.56E-04
5b	4.58E-04	0.75	0.75	4.60E-04
5c	4.63E-04	0.99	0.99	4.72E-04
5d	4.70E-04	1.24	1.24	4.84E-04
5e	4.76E-04	1.50	1.50	4.82E-04
5f	4.89E-04	2.00	2.00	4.94E-04
5g	5.03E-04	2.50	2.50	5.06E-04
5h	5.14E-04	3.00	3.00	5.21E-04
5i	5.29E-04	3.50	3.50	5.28E-04
5j	5.40E-04	4.00	4.00	5.43E-04
6a	9.98E-04	4.00	4.00	1.00E-03

Note: pH<sub>25°C</sub> ~5.5.

Table S3. Compositions of ammonia-bearing solutions used in XAS measurements.

Sample #	Cu <sup>+</sup> (m)	NH <sub>4</sub> <sup>+</sup> (m)	NH <sub>3</sub> (m)	Cl <sup>-</sup> (m)	NH <sub>3</sub> /Cu ratio
CuNH3_01	4.53E-03	2.30E-01	2.29E-01	0.6921	50.51
CuNH3_02	4.47E-03	1.13E-01	1.12E-01	0.4512	25.08
CuNH3_03	9.22E-03	2.33E-01	2.31E-01	0.9308	25.08
CuNH3_04	5.45E-03	8.33E-02	8.28E-02	4.2736	15.19
CuNH3_05	1.09E-02	9.07E-02	9.01E-02	4.1536	8.30
CuNH3_06	1.30E-02	5.18E-02	5.16E-02	4.4407	3.96
CuNH3_07	1.86E-02	3.17E-02	3.15E-02	3.9543	1.69
CuNH3_08	1.74E-02	1.71E-02	1.70E-02	4.0485	0.98
CuNH3_09	1.81E-02	6.87E-03	6.83E-03	4.1131	0.38
CuNH3_10	1.68E-02	4.03E-02	4.01E-02	3.9018	2.39

Note: pH<sub>25°C</sub> ~ 9.25.

Table S4. Compositions of Cu(I)-NH<sub>3</sub>-Cl solutions used for UV-Vis measurements. Provide both nitrogen compound concentrations, as in Table S3.

Sample	Cu <sup>+</sup> (m)	Cl <sup>-</sup> (m)	Na <sup>+</sup> (m)	N <sub>tot</sub> * (m)	pH <sub>25°C</sub>
6a	4.83E-04	4.00	3.99	4.38E-03	9.17
6b	4.82E-04	4.00	3.99	8.22E-03	9.20
6c	4.82E-04	4.00	3.99	1.57E-02	9.22
6d	5.73E-04	4.00	3.98	2.99E-02	9.26
6e	4.82E-04	4.00	3.97	4.76E-02	9.26
6f	4.82E-04	4.00	3.97	6.33E-02	9.27
6g	4.89E-04	4.00	3.96	7.85E-02	9.27
6h	4.83E-04	4.00	3.95	9.88E-02	9.28
6i	4.85E-04	4.01	3.94	1.18E-01	9.28
6j	5.05E-04	4.01	3.93	1.37E-01	9.29
6k	4.83E-04	4.01	3.92	1.58E-01	9.28
7a	2.33E-04	0.59	0.57	3.07E-02	9.31
7b	2.42E-04	0.97	0.95	3.02E-02	9.31
7c	2.45E-04	1.49	1.47	3.04E-02	9.32
7d	2.52E-04	2.00	1.98	3.02E-02	9.31
7e	2.59E-04	2.51	2.49	3.01E-02	9.28
7f	2.66E-04	3.01	3.00	2.99E-02	9.28
7g	2.72E-04	3.51	3.49	2.98E-02	9.28
7h	2.78E-04	4.00	3.99	2.98E-02	9.27
7i	2.85E-04	4.49	4.47	2.96E-02	9.28
7j	2.91E-04	4.97	4.95	2.94E-02	9.26
8a	2.33E-04	0.63	0.60	5.15E-02	9.34
8b	2.33E-04	0.98	0.95	5.16E-02	9.35
8c	2.38E-04	1.49	1.46	5.14E-02	9.35
8d	2.48E-04	1.99	1.96	5.08E-02	9.35
8e	2.52E-04	2.51	2.48	5.08E-02	9.34
8f	2.60E-04	3.02	2.99	5.05E-02	9.34
8g	2.64E-04	3.51	3.48	5.05E-02	9.34
8h	2.71E-04	4.00	3.98	5.01E-02	9.33

\* N<sub>tot</sub> = [NH<sub>4</sub><sup>+</sup>] + [NH<sub>3</sub>]

**Figure S1.** UV-Vis data collected for the Cu(I)-Cl<sup>-</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> system. (a) plot of the solution compositions in Cl<sup>-</sup> versus S<sub>2</sub>O<sub>3</sub><sup>2-</sup> space. The boxes I and II outline subsets of solutions whose spectra are plotted in Figure 6. (b) Principal component analysis of the whole spectral dataset.

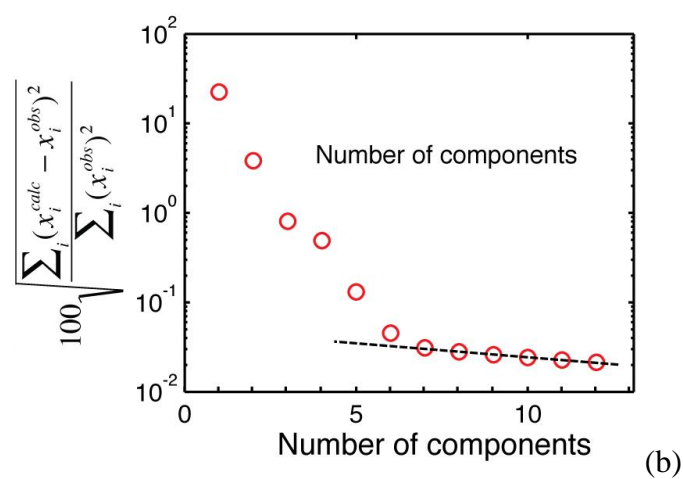
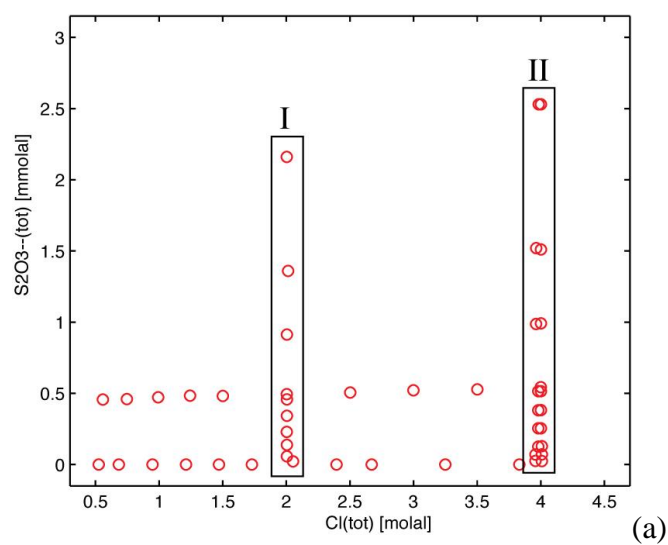


Figure S2. Residual space resulting from the fitting of the thiosulfate-chloride dataset at 25°C, as a function of the formation constants for  $[\text{Cu}(\text{S}_2\text{O}_3)_3]^{3-}$ ,  $[\text{CuCl}(\text{S}_2\text{O}_3)(\text{H}_2\text{O})]^{2-}$  and  $\text{Cu}(\text{S}_2\text{O}_3)\text{Cl}_2^{4-}$ .

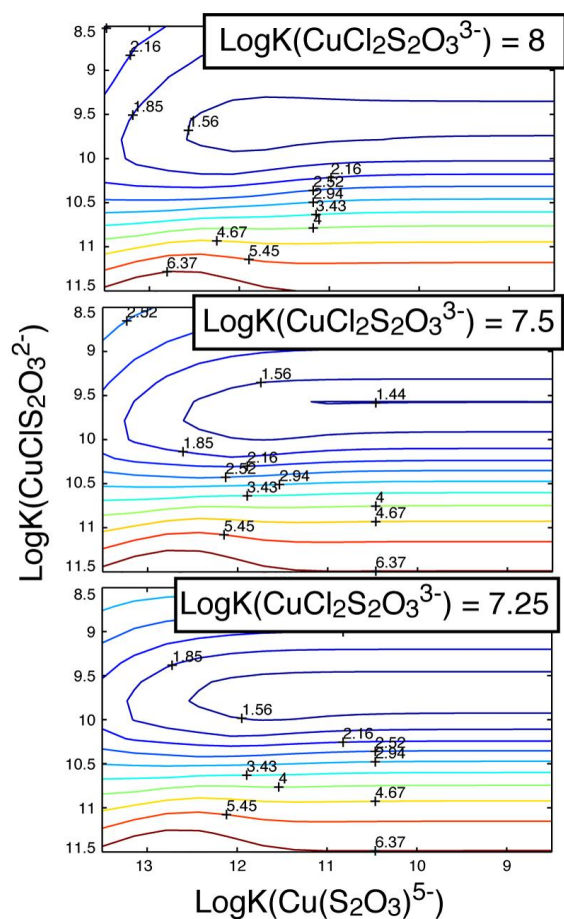


Figure S3. Solution compositions and results of PCA calculations for UV-Vis data in the Cu(I)-NH<sub>3</sub>(aq)-Cl system. (a) Total nitrogen and chloride concentrations in experimental solutions. The boxes I, II outline solutions whose spectra are plotted in Figure 13. (b) Principal component analysis of the whole spectral dataset.

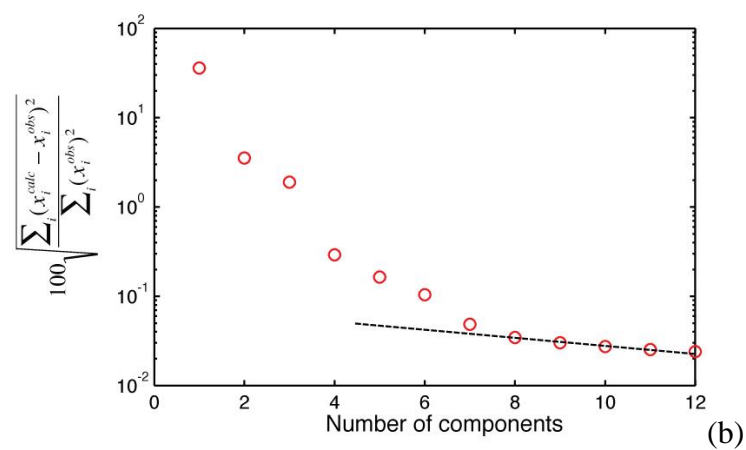
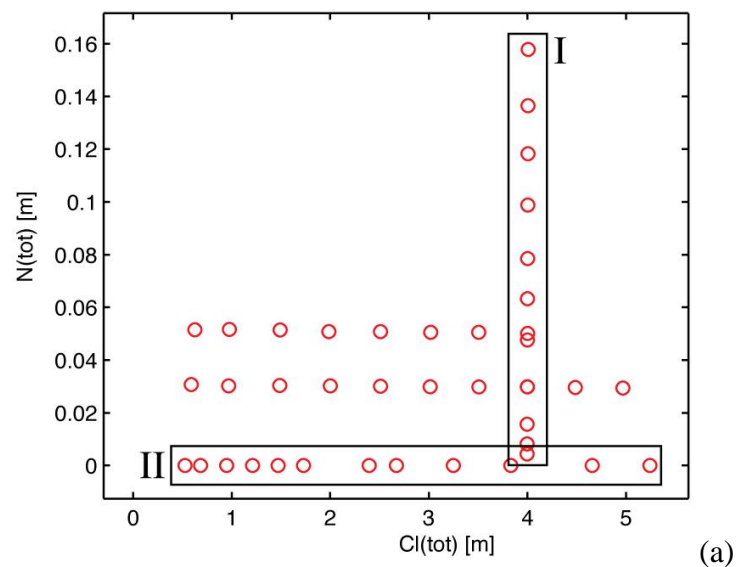




Figure S4. Residual space resulting from the fitting of the  $\text{NH}_3$ -chloride dataset at 25°C. The isoline at 0.733 represents the 90% confidence level.

