Supplementary Information for:

" Blueprint XAS: A Matlab-based toolbox for the fitting and analysis of XAS spectra ".

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S1. Curve fitting and Matlab built-in functions

Blueprint XAS makes use of several Matlab built-in functions as part of the curve-fitting toolbox for Matlab. Following is a brief description of these functions.

1) **Function fittype.** It generates an object with a full description of the evaluation function and its parameters.

2) **Function fitoptions:** It generates a structure containing all of the details on the parameters required to compute the fit. Several fit-option parameters are contained in this structure and passed on to Matlab through Blueprint XAS:

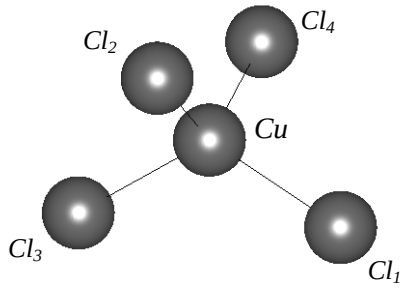
- "Algorithm" corresponds to the Non-Linear Least-Squares (NLLS) curve fitting method to be used. Three different NLLS algorithms are available in Matlab and are all accessible through Blueprint XAS: a) Trust-region, b) Levenberg-Marquardt and c) Gauss-Newton.
- "Exclude" is a vector of logicals of the same size as the data. Regions of the spectrum that are excluded for the fit are assigned values of one (or "true") in the corresponding matrix elements of the exclusion vector.
- "DiffMinChange" and "DiffMaxChange" correspond, respectively to the minimum and maximum change in the finite differences gradient.
- "Lower" and "Upper" are vectors containing the lower and upper bounds for every parameter in the evaluation model. The "StartPoint" vector, which is another field of the “fitoptions” structure contains an initial guess but is only accessible trough blueprint XAS if the type of job is chosen to be "manual". Otherwise, internally, after the Monte-Carlo search subroutine selects the best start point out of a thousand (Delgado-Jaime &

Kennepohl, 2010), is when this vector is passed on to the “fitoptions” structure prior to the computation of every fit.

- "MaxFunEvals", the maximum number of function evaluations, correspond to one of the criteria used by Matlab to exit the fitting algorithm. Another criteria used is "MaxIter", the number of maximum iterations allowed inside the fitting algorithm. Additionally, termination tolerance parameters in the evaluation function (TolFun), and in the coefficients (TolX) are used as the criteria for convergence by Matlab.
- "Robust" allows the use of a weighting factor for each data point as a way to systematically reduce the influence of possible outliers in the fitting procedure.
- "Weights" is a vector with values between 0 and 1 that explicitly allows the user to deliberately impose a different weighting influence to the fitting procedure in different regions of the data.

3) **Function fit**. It uses the "fittype" object as well as the "fitoptions" structure to fit the model to the data. The output of this function includes a "cfit" object from which the fitted parameters, their corresponding confidence intervals (at the level specified), and the evaluation function at the given data points can be retrieved. Additionally, the goodness-of-fit parameters along with the residuals are also obtained and passed on to Blueprint XAS in the output. The interested reader can refer to the Matlab documentation online to learn more about these parameters (Mathworks, 2009, Moler, 1999).

Table S2 Internal coordinates for $CuCl_4^{2-}$ moiety in the crystal structure of $(NEt_4)_2CuCl_4 \cdot {}^1/_2H_2O$ used in the time dependent DFT calculation of the first 20 transition lines from the 1s core electron of each of the Cl atoms to the empty molecular orbitals of $CuCl_4^{2-}$.



Bond distances (Å)		Bond Angles (deg)		Dihedral angles (deg)	
Cu-Cl_1	2.2302	Cl_1-Cu-Cl_2	104.24	Cl_2-Cu-Cu-Cl_3	243.62
Cu-Cl_2	2.2302	Cl_1-Cu-Cl_3	120.53	Cl_2-Cu-Cu-Cl_4	243.62
Cu-Cl_3	2.2302	Cl_1-Cu-Cl_4	104.24		
Cu-Cl_4	2.2302				

Table S3 calculated energies and oscillator strengths for the first 20 transition lines originated from the 1s orbital of chlorine atoms 1 and 2 of tetragonal $CuCl_4^{2-}$ (see **Table S2**).

Transition line, i	Energy, E_i	Oscillator strength, s_i	Energy, E_i	Oscillator strength, s_i
	Chlorine atom # 1		Chlorine atom # 2	
1	2733.7	0.001938	2733.7	6.97×10^{-5}
2	2738	5.54×10^{-8}	2738	3.78×10^{-7}
3	2738	2.49×10^{-6}	2738	1.86 x10-^{5}
4	2740.7	1.20×10^{-5}	2740.7	0.000165
5	2740.8	3.28×10^{-5}	2740.8	0.000433
6	2741.4	0.000142	2741.4	1.01×10^{-5}
7	2741.4	0.000706	2741.4	4.75×10^{-5}
8	2741.8	8.04×10^{-5}	2741.8	1.51×10^{-5}
9	2741.8	8.53×10^{-5}	2741.8	1.54×10^{-5}
10	2741.9	0.000464	2741.9	9.51×10^{-5}
11	2741.9	0.000459	2741.9	6.96×10^{-5}
12	2744.2	1.65×10^{-5}	2744.2	8.25×10^{-5}
13	2744.3	7.28×10^{-5}	2744.3	0.000393
14	2744.7	2.46×10^{-5}	2744.7	6.00×10^{-5}
15	2744.7	2.14×10^{-5}	2744.7	8.21×10^{-5}
16	2744.7	0.000526	2744.7	0.000131
17	2744.8	0.001123	2744.8	0.00094
18	2744.8	0.001201	2744.8	0.001293
19	2744.8	0.002418	2744.8	6.49×10^{-5}
20	2744.8	1.21×10^{-5}	2744.8	5.73×10^{-5}

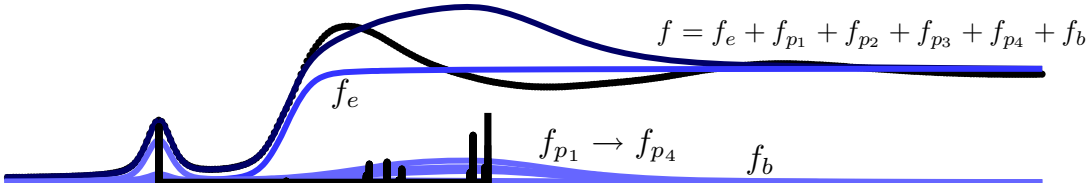
Table S4 calculated energies and oscillator strengths for the first 20 transition lines originated from the 1s orbital of chlorine atoms 3 and 4 of tetragonal $CuCl_4^{2-}$ (see **Table S2**).

Transition line, i	Energy, E_i	Oscillator strength, s_i	Energy, E_i	Oscillator strength, s_i
	Chlorine atom # 3		Chlorine atom # 4	
1	2733.7	0.000346	2733.7	0.0002
2	2738	1.16×10^{-6}	2738	9.26×10^{-7}
3	2738	4.72×10^{-5}	2738	3.77×10^{-5}
4	2740.7	0.000243	2740.7	0.000219
5	2740.8	0.000638	2740.8	0.000568
6	2741.4	4.74E-05	2741.4	3.13×10^{-5}
7	2741.4	0.000237	2741.4	0.000149
8	2741.8	6.00×10^{-6}	2741.8	8.04×10^{-6}
9	2741.8	9.60×10^{-6}	2741.8	1.14×10^{-5}
10	2741.9	4.13×10^{-5}	2741.9	4.87×10^{-5}
11	2741.9	5.28×10^{-5}	2741.9	5.75×10^{-5}
12	2744.2	0.00034	2744.2	0.000256
13	2744.3	0.001643	2744.3	0.001204
14	2744.7	3.42×10^{-5}	2744.7	3.05×10^{-5}
15	2744.7	6.09×10^{-5}	2744.7	7.38×10^{-5}
16	2744.7	1.60×10^{-5}	2744.7	0.000101
17	2744.8	0.00084	2744.8	0.000776
18	2744.8	0.000526	2744.8	0.000782
19	2744.8	0.000289	2744.8	1.34×10^{-5}
20	2744.8	0.000184	2744.8	0.000132

Table S5 'fitoptions' parameters used in the fitting of the Cl K-edge XAS data set of $(NEt_4)_2CuCl_4$, based on computed transition lines of **Tables S3** and **S4**.

Parameter Name	Value	Parameter Name	Value
Algorithm	Trust-Region	**Robust**	On
DiffMinChange	10^{-8}	**DiffMaxChange**	0.1
MaxIter	2,500	**MaxFunEvals**	750
TolFun	10^{-6}	**TolX**	10^{-6}

Figure S6: Evaluation function for the fitting of the Cl K-edge XAS data set of $(NEt_4)_2CuCl_4$, based on computed transition lines of **Tables S3** and **S4**. Function denoted by '*u*' corresponds to the Heaviside's unit step function.



$$f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)$$

$$C_G = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1/ln2}\right)\right]$$

$$C_L = \frac{1}{2}\arctan\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1}\right) + \frac{1}{\pi}$$

$$f_{p_1-p_4} = I_2 \cdot I_1 \cdot \sum_i^{20} s_i \cdot (G_2 \cdot F_{G_{p_1-p_4}} + (1 - G_2) \cdot L_{p_1-p_4})$$

$$F_{G_{p_1-p_4}} = \sqrt{\frac{ln2}{W_{f_M}^2 \pi}} e^{-\frac{ln2(x-E_i-O_2)^2}{W_{f_M}^2}}$$

$$L_{p_1-p_4} = \frac{1}{\pi} \times \frac{W_{f_M}}{(\mathrm{x} - \mathrm{E_i} - \mathrm{O}_2)^2 + W_{f_M}^2}$$

$$W_{f_M} = W_2 \cdot u(O_1 - B_1 - x) + \left(W_2 + (E_i + O_2 + B_1 - O_1) \times \frac{W_3 - W_2}{B_1 + B_2}\right) \cdot u(x - O_1 + B_1) \cdot u(O_1 + B_2 - x) + W_3 \cdot u(x - O_1 + B_2)$$

$$f_b = f_1 \frac{1}{1 + e^{\frac{(x-O_1)ln3}{W_1}}} + f_2 \frac{1}{1 + e^{\frac{(O_1-x)ln3}{W_1}}}$$

$$f_1 = m_1 \cdot x + YI$$

$$f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)$$

References

Delgado-Jaime, M. U. & Kennepohl, P. (2010). *J Synchrotron Radiation*, **17** (companion manuscript).

Mathworks (2009). *fitoptions (Curve fitting Toolbox),* http://www.mathworks.com/access/helpdesk/help/toolbox/curvefit/index.html?/access/helpdesk/help/toolbox/curvefit/f2-17602.html.

Moler, C. (1999). *Optimally Speaking: Optimization Toolbox features new methods for large-scale problems,* http://www.mathworks.com/company/newsletters/news_notes/clevescorner/sm99cleve.html.