Supplementary Material

Table S1. a/ Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $Cu(Me_2SO)_6(ClO_4)_2 \cdot 2Me_2SO$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, b/ anisotropic displacement parameters ($Å^2x\ 10^3$) for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U_{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U_{12}\,]$ and c/ hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x\ 10^3$) for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$

Table S2. Interatomic bond distances (Å) and angles (^{o}) in the structure of hexakis-(dimethylsulfoxide)copper(II) perchlorate didimethylsulfoxide.

Table S3. Fractional atomic coordinates and equivalent isotopic displacement coefficients ($Å^2$) for the structure of hexakis(dimethylsulfoxide) tetrakis(dimethylsulfoxide)-bishydroxocopper(II) perchlorate.

Table S4. Interatomic bond distances (Å) and angles (^{o}) in the structure of tetrakis-(dimethylsulfoxide)bishydroxocopper(II) perchlorate.

Figure S1. The Fourier transforms and the fit of solid hexaaquacopper(II) bromate (offset 10.5), solid hexaaquacopper(II) hexafluorosilicate (offset 9.0), an aqueous solution of copper(II) perchlorate (offset 7.5), solid hexakis(pyridine-1-oxide)copper(II) perchlorate (offset 6.0), solid tetrakis(pyridine-1-oxide)copper(II) perchlorate (offset 4.5), solid hexakis(dimethylsulfoxide)copper(II) perchlorate (offset 3.0), dimethylsulfoxide solution of copper(II) perchlorate (offset 1.5) and *N,N'*-dimethylpropyleneurea solution of copper(II) trifluoromethanesulfonate.

Figure S2. The fit and the individual contribution of the different scattering paths of the EXAFS data of

a/ solid hexaaquacopper(II) bromate, solid line - experimental data and dashed line - model. Individual contributions: $Cu\text{-}O_{eq}$ single scattering - solid line (offset -4), $Cu\text{-}O_{ax}$ single scattering - dashed line (offset -10), $Cu\text{-}O_{eq}\text{-}O_{eq}$ linear multiple scattering - dotted line (offset -12), $Cu\text{-}O_{eq}\text{-}Cu\text{-}O_{eq}$ linear multiple scattering - dash-dotted line (offset -14) and $Cu\text{-}O_{eq}\text{-}Cu\text{-}O_{eq}$ linear multiple scattering - dash-dotted line (offset -16).

b/ solid hexaaquacopper(II) hexafluorosilicate, solid line - experimental data and dashed line - model. Individual contributions: $Cu\text{-}O_{eq}$ single scattering - solid line (offset -4), $Cu\text{-}O_{ax}$ single scattering - dashed line (offset -10), $Cu\text{-}O_{eq}\text{-}O_{eq}$ linear multiple scattering - dotted line (offset -12), $Cu\text{-}O_{eq}\text{-}Cu\text{-}O_{eq}$ linear multiple scattering - dash-dotted line (offset -14) and $Cu\text{-}O_{eq}\text{-}Cu\text{-}O_{eq}$ linear multiple scattering - dash-dotted line (offset -16).

c/ aqueous solution of copper(II) perchlorate, solid line - experimental data and dashed line - model. Individual contributions: $Cu\text{-}O_{eq}$ single scattering - solid line (offset -4), $Cu\text{-}O_{ax}$ single scattering - dashed line (offset -10), $Cu\text{-}O_{eq}\text{-}O_{eq}$ linear multiple scattering - dotted

line (offset -12), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -14) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -16).
d/ solid hexakis(pyridine-1-oxide)copper(II) perchlorate, solid line - experimental data and dashed line - model. Individual contributions: Cu-O_{eq} single scattering - solid line (offset -4), Cu···N_{eq} single scattering - dashed line (offset -10), Cu-O_{eq}-N_{eq} three-leg scattering path - dotted line (offset -12), Cu-O_{eq}-O_{eq} linear multiple scattering - dotted line (offset -14), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -16) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -18).
e/ solid tetrakis(pyridine-1-oxide)copper(II) perchlorate, solid line - experimental data and dashed line - model. Individual contributions: Cu-O_{eq} single scattering - solid line (offset -4), Cu···N_{eq} single scattering - dashed line (offset -10), Cu-O_{eq}-N_{eq} three-leg scattering path - dotted line (offset -12), Cu-O_{eq}-O_{eq} linear multiple scattering - dotted line (offset -14), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -16) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -18).
f/ solid hexakis(dimethylsulfoxide)copper(II) perchlorate, solid line - experimental data and dashed line - model. Individual contributions: Cu-O_{eq} single scattering - solid line (offset -4), Cu-O_{ax} single scattering - dashed line (offset -12), Cu···S_{eq} single scattering - dotted line (offset -16), Cu-O_{eq}-S_{eq} three-leg scattering path - dash-dotted line (offset -20), Cu-O_{eq}-O_{eq} linear multiple scattering - dotted line (offset -22), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -24) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -26).
g/ dimethylsulfoxide solution of copper(II) perchlorate, solid line - experimental data and dashed line - model. Individual contributions: Cu-O_{eq} single scattering - solid line (offset -4), Cu···S_{eq} single scattering - dotted line (offset -12), Cu-O_{eq}-S_{eq} three-leg scattering path - dash-dotted line (offset -16), Cu-O_{eq}-O_{eq} linear multiple scattering - dotted line (offset -18), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -20) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -22).
h/ *N,N'*-dimethylpropyleneurea solution of copper(II) trifluoromethanesulfonate, solid line - experimental data and dashed line - model. Individual contributions: Cu-O single scattering - solid line (offset -4), Cu···C single scattering - dotted line (offset -10), Cu-O_{eq}-O_{eq} linear multiple scattering - dotted line (offset -12), Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -14) and Cu-O_{eq}-Cu-O_{eq} linear multiple scattering - dash-dotted line (offset -16).

Figure S3. Normalized absorption edges of the studied samples. A help line is inserted at 8998 eV.

Table S1a. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cu(1)	5000	0	0	49(1)
S(2)	2915(2)	-60(2)	2758(2)	82(1)
S(3)	6521(2)	72(2)	1935(2)	62(1)
S(1)	5201(2)	-3192(2)	1410(2)	68(1)
S(4)	822(3)	-4063(2)	1158(2)	97(1)
Cl(1)	2841(2)	2757(2)	4397(2)	81(1)
O(1)	6036(4)	-1719(4)	556(4)	60(1)
O(2)	3329(5)	-941(4)	1991(4)	76(1)
O(3)	6231(4)	990(4)	615(4)	65(1)
O(4)	-157(6)	-3158(5)	445(5)	112(2)
O(13)	3223(7)	3429(6)	3005(5)	132(2)
O(12)	4044(9)	2242(8)	4772(7)	187(3)
O(11)	2441(10)	3725(9)	4892(8)	194(3)
O(14)	1760(10)	1678(8)	4953(7)	204(4)
C(1A)	6262(10)	-4181(7)	602(8)	118(3)
C(1B)	5665(10)	-3870(7)	2885(7)	108(3)
C(2A)	2269(10)	-1322(9)	4455(7)	127(3)
C(2B)	1269(8)	581(8)	2570(8)	102(3)
C(3A)	6823(9)	1298(7)	2518(7)	95(2)
C(3B)	8317(7)	-359(7)	1461(7)	80(2)
C(4A)	-168(10)	-5695(8)	2269(10)	140(4)
C(4B)	933(9)	-3492(8)	2351(8)	102(3)

Table 1b. Anisotropic displacement parameters ($Å^2x\ 10^3$) for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	41(1)	56(1)	46(1)	-20(1)	-15(1)	8(1)
S(2)	56(1)	112(2)	90(1)	-60(1)	-16(1)	3(1)
S(3)	50(1)	76(1)	50(1)	-20(1)	-16(1)	5(1)
S(1)	54(1)	64(1)	77(1)	-23(1)	-23(1)	4(1)
S(4)	96(2)	86(1)	103(2)	-37(1)	-32(1)	13(1)
Cl(1)	79(2)	83(1)	64(1)	-21(1)	-18(1)	7(1)
O(1)	43(3)	65(3)	69(3)	-23(2)	-22(2)	8(2)
O(2)	76(3)	73(3)	80(3)	-39(2)	-20(3)	5(2)
O(3)	63(3)	71(3)	53(3)	-19(2)	-22(2)	9(2)
O(4)	127(5)	80(3)	122(4)	-16(3)	-71(4)	17(3)

O(13)	149(6)	143(5)	65(4)	-18(3)	-28(4)	9(4)
O(12)	148(7)	234(8)	154(6)	-53(5)	-76(6)	97(6)
O(11)	222(9)	200(7)	182(7)	-126(6)	-40(7)	58(7)
O(14)	190(9)	207(7)	144(6)	-32(5)	-13(6)	-118(7)
C(1A)	135(8)	77(5)	133(7)	-58(5)	-14(6)	5(5)
C(1B)	147(9)	79(5)	86(6)	-15(4)	-52(6)	-3(5)
C(2A)	135(9)	167(8)	80(6)	-49(6)	-43(6)	25(7)
C(2B)	63(6)	137(7)	109(6)	-60(5)	-26(5)	25(5)
C(3A)	103(7)	111(6)	85(5)	-53(5)	-34(5)	21(5)
C(3B)	59(5)	82(5)	93(5)	-31(4)	-28(4)	13(4)
C(4A)	135(9)	91(6)	175(9)	-13(6)	-91(8)	-6(6)
C(4B)	101(7)	102(5)	122(7)	-59(5)	-51(6)	25(5)

Table 1c. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$.

	x	*y*	*z*	U_{eq}
H(1AA)	6119	-3922	-254	177
H(1AB)	5971	-5174	1171	177
H(1AC)	7268	-3980	454	177
H(1BA)	5166	-3429	3448	162
H(1BB)	6692	-3682	2654	162
H(1BC)	5392	-4874	3369	162
H(2AA)	3061	-1785	4726	191
H(2AB)	1574	-2010	4556	191
H(2AC)	1816	-865	5015	191
H(2BA)	1441	1308	1661	153
H(2BB)	854	964	3203	153
H(2BC)	612	-179	2743	153
H(3AA)	5925	1650	2822	142
H(3AB)	7508	2072	1791	142
H(3AC)	7199	839	3257	142
H(3BA)	8348	-1038	1111	120
H(3BB)	8636	-753	2241	120
H(3BC)	8942	481	775	120
H(4AD)	-327	-6159	1762	210
H(4AE)	-1084	-5564	2806	210
H(4AF)	358	-6265	2855	210
H(4BA)	1467	-2570	1884	152
H(4BB)	1417	-4146	2934	152
H(4BC)	-26	-3447	2886	152

Table S2. Bond lengths [Å] and angles [°] for $Cu(OSMe_2)_6(ClO_4)_2 \cdot 2Me_2SO$.

Cu(1)-O(1)	1.990(4)
Cu(1)-O(1)#1	1.990(4)
Cu(1)-O(3)	2.083(4)
Cu(1)-O(3)#1	2.083(4)
Cu(1)-O(2)#1	2.182(4)
Cu(1)-O(2)	2.182(4)
S(2)-O(2)	1.507(4)
S(2)-C(2A)	1.746(8)
S(2)-C(2B)	1.757(7)
S(3)-O(3)	1.519(4)
S(3)-C(3B)	1.769(6)
S(3)-C(3A)	1.770(7)
S(1)-O(1)	1.527(4)
S(1)-C(1B)	1.738(7)
S(1)-C(1A)	1.783(7)
S(4)-O(4)	1.496(5)
S(4)-C(4A)	1.732(7)
S(4)-C(4B)	1.760(7)
Cl(1)-O(11)	1.362(7)
Cl(1)-O(14)	1.368(7)
Cl(1)-O(13)	1.375(5)
Cl(1)-O(12)	1.386(7)
O(1)-Cu(1)-O(1)#1	180.0(2)
O(1)-Cu(1)-O(3)	90.97(15)
O(1)#1-Cu(1)-O(3)	89.03(15)
O(1)-Cu(1)-O(3)#1	89.03(15)
O(1)#1-Cu(1)-O(3)#1	90.97(15)
O(3)-Cu(1)-O(3)#1	180.00(18)
O(1)-Cu(1)-O(2)#1	90.32(15)
O(1)#1-Cu(1)-O(2)#1	89.68(15)
O(3)-Cu(1)-O(2)#1	86.83(16)
O(3)#1-Cu(1)-O(2)#1	93.17(16)
O(1)-Cu(1)-O(2)	89.68(15)
O(1)#1-Cu(1)-O(2)	90.32(15)
O(3)-Cu(1)-O(2)	93.17(16)
O(3)#1-Cu(1)-O(2)	86.83(16)
O(2)#1-Cu(1)-O(2)	180.0(2)
O(2)-S(2)-C(2A)	103.4(3)
O(2)-S(2)-C(2B)	106.8(3)
C(2A)-S(2)-C(2B)	98.9(4)
O(3)-S(3)-C(3B)	106.0(3)
O(3)-S(3)-C(3A)	103.7(3)
C(3B)-S(3)-C(3A)	98.6(4)

O(1)-S(1)-C(1B)	104.5(3)
O(1)-S(1)-C(1A)	101.9(3)
C(1B)-S(1)-C(1A)	99.2(4)
O(4)-S(4)-C(4A)	106.3(4)
O(4)-S(4)-C(4B)	107.0(3)
C(4A)-S(4)-C(4B)	99.0(4)
O(11)-Cl(1)-O(14)	111.2(6)
O(11)-Cl(1)-O(13)	109.1(4)
O(14)-Cl(1)-O(13)	111.4(4)
O(11)-Cl(1)-O(12)	105.0(5)
O(14)-Cl(1)-O(12)	110.1(5)
O(13)-Cl(1)-O(12)	109.7(4)
S(1)-O(1)-Cu(1)	120.9(2)
S(2)-O(2)-Cu(1)	117.8(2)
S(3)-O(3)-Cu(1)	116.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z