Supporting information

Crystal Structure and Carrier Transport Properties of a New 3D Mixed-Valence Cu(I)-Cu(II) Coordination Polymer Including Pyrrolidine Dithiocarbamate Ligand

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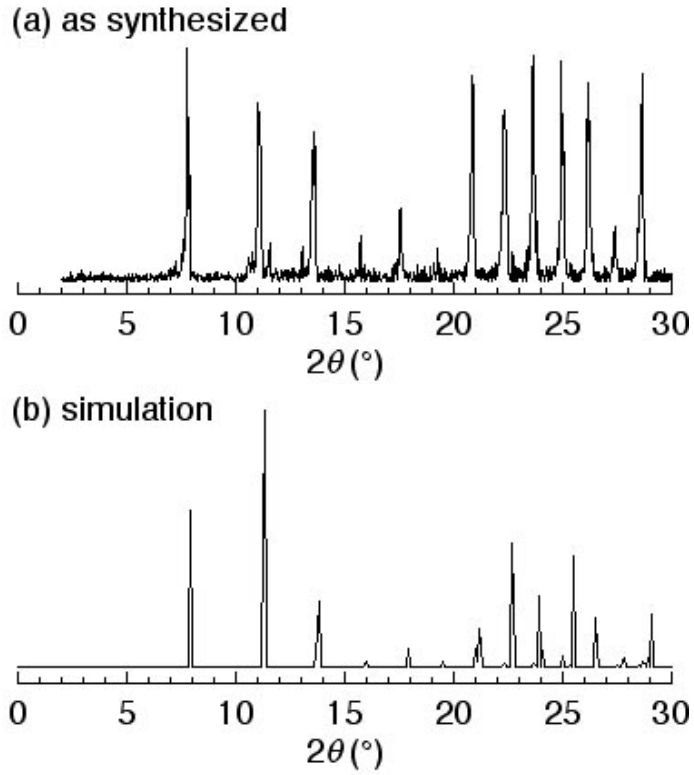

Figure S1. Comparison of XRPD patterns of product **1** (a) with the respective calculated ones (b) form the single-crystal data.

Table S1. Estimated parameters (R_1, C_1, R_2, C_2, R_3, CPE_3-A and CPE_3-α) by the fittings to the impedance data of **1** at different temperatures with the equivalent circuit in the inset of Figure 6 using ZView software, where R_1, R_2 and R_3 are the resistances, CPE_3-A is the parameter concerned with the capacitance, and CPE_3-α is corresponding to the dispersion of the relaxation time of the electrode interface, respectively; the CPE impedance is given by the relationship: $Z_{CPE} = 1/[A(j\omega)^{\alpha}]$, and for $\alpha = 1$ the CPE describes an ideal capacitor ($A = C$).

T (K)	R_1 (Ω)	C_1 (F)	R_2 (Ω)	C_2 (F)	R_3 (Ω)	CPE_3-A	CPE_3-a	χ^2
250	3.59E+05	5.24E-11	1.82E+06	7.18E-11	1.80E+08	3.88E-11	0.97654	0.002277
255	3.33E+05	4.73E-11	1.65E+06	7.84E-11	1.93E+08	4.16E-11	0.9738	0.0019584
260	2.35E+05	4.80E-11	1.16E+06	8.05E-11	1.56E+08	4.48E-11	0.96724	0.001954

265	2.05E+05	4.69E-11	9.49E+05	9.05E-11	1.64E+08	4.86E-11	0.96142	0.0016443
270	1.59E+05	4.94E-11	6.54E+05	1.04E-10	1.34E+08	5.41E-11	0.95008	0.0011515
275	1.25E+05	4.91E-11	5.14E+05	1.09E-10	1.04E+08	5.73E-11	0.94643	0.0011083
280	1.04E+05	4.87E-11	4.32E+05	1.19E-10	9.28E+07	6.20E-11	0.94117	0.0017478
285	78234	5.11E-11	3.03E+05	1.33E-10	8.41E+07	6.87E-11	0.93136	0.0013741
290	60215	5.44E-11	2.11E+05	1.53E-10	7.37E+07	7.56E-11	0.92229	0.00096505
295	47979	5.72E-11	1.55E+05	1.83E-10	6.33E+07	8.48E-11	0.91238	0.0012443
300	40506	5.79E-11	1.39E+05	2.07E-10	5.61E+07	9.17E-11	0.90762	0.0011505

Table S2. Calculated electric conductivity σ and dielectric constant ε' from the parameters in Table S1 by using the following relationships: $\sigma = 1/R \times d/S$ and $\varepsilon' \approx A/\varepsilon_0 \times d/S$, where d is the thickness of the pellet sample, S is the electrode area and ε_0 is the permittivity of vacuum, 8.855×10^{-12} F/m. The σ_1 and σ_2 values are corresponding to the electric conductivity of the bulk sample and grain boundary of **1**, respectively.

	σ_1 (S cm^{-1})	ε_1	σ_2 (S cm^{-1})	ε_2
250	5.90E-08	12.541	1.16E-08	17.165
255	6.36E-08	11.314	1.29E-08	18.753
260	9.03E-08	11.489	1.82E-08	19.26
265	1.04E-07	11.221	2.23E-08	21.65
270	1.34E-07	11.809	3.24E-08	24.972
275	1.69E-07	11.742	4.12E-08	26.145
280	2.04E-07	11.644	4.90E-08	28.537
285	2.71E-07	12.221	6.98E-08	31.718
290	3.52E-07	13.01	1.00E-07	36.598
295	4.41E-07	13.692	1.37E-07	43.869
300	5.23E-07	13.85	1.53E-07	49.538

Table S3. Crystal Data and Structure Refinement Parameters for **1**.

Empirical Formula	$C_{21}H_{33}N_4S_8Cu_6Br_4Cl_3$

Formula Weight	1405.25
Crystal System	tetragonal
Lattice Parameters	a = 15.6452(5) Å
	c = 15.9953(6) Å
	V = 3915.2(2) Å^3
Space Group	I4$_1$/a (#88)
Z value	4
D_{calc}	2.384 g/cm^3
F_{000}	2720.00
μ(MoKα)	79.515 cm^{-1}
No. Observations (All reflections)	2236
No. Variables	109
Reflection/Parameter Ratio	20.51
Residuals: R_1 ($I > 2.00\ \sigma(I)$) [a]	0.0365
Residuals: R (All reflections)	0.0385
Residuals: wR_2 (All reflections) [b]	0.0872
Goodness of Fit Indicator	1.045
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	2.78 e/Å^3
Minimum peak in Final Diff. Map	-2.04 e/Å^3

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[a] $R_1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S4. Atomic coordinates and B_{iso}/B_{eq} and occupancy for **1.**

atom	x	y	z	B_{eq}	occ
Br1	0.22059(2)	0.52393(3)	0.00067(3)	1.445(9)	
Cu1	0.5000	0.5000	0.0000	1.181(12)	1/2
Cu2	0.30162(3)	0.53620(3)	0.13061(3)	1.364(11)	
Cl1	0.9235(2)	0.32420(19)	0.08138(19)	7.54(9)	3/4
S1	0.57147(6)	0.58857(6)	0.09172(6)	1.333(16)	
S2	0.43655(6)	0.46530(6)	0.12531(6)	1.230(15)	
N1	0.5064(2)	0.5628(2)	0.2450(2)	1.30(5)	

C1	0.5059(2)	0.5416(2)	0.1667(2)	1.17(5)	
C2	0.5603(2)	0.6318(2)	0.2811(2)	1.59(6)	
C3	0.5296(3)	0.6373(3)	0.3714(3)	2.25(7)	
C4	0.4982(3)	0.5471(3)	0.3906(2)	2.25(8)	
C5	0.4536(2)	0.5210(3)	0.3101(2)	1.73(6)	
C6	1.0000	0.2500	0.1250	10.5(7)	1/4

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S5. Anisotropic displacement parameters for **1.**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.0151(2)	0.0205(2)	0.0193(2)	0.00190(14)	-0.00176(14)	-0.00510(15)
Cu1	0.0124(3)	0.0158(3)	0.0167(3)	0.0007(2)	0.0008(2)	0.0009(2)
Cu2	0.0173(2)	0.0166(2)	0.0179(2)	-0.00086(18)	-0.00034(19)	-0.00068(19)
Cl1	0.174(3)	0.0541(15)	0.0581(16)	-0.0517(19)	-0.0107(19)	0.0012(12)
S1	0.0130(4)	0.0191(4)	0.0186(4)	-0.0019(3)	-0.0003(3)	0.0031(3)
S2	0.0141(4)	0.0144(4)	0.0182(4)	-0.0010(3)	0.0017(3)	-0.0012(3)
N1	0.0131(15)	0.0160(16)	0.0202(17)	0.0009(12)	-0.0001(12)	0.0006(13)
C1	0.0107(16)	0.0134(17)	0.0204(19)	0.0012(13)	-0.0009(14)	0.0010(14)
C2	0.0171(19)	0.0165(18)	0.027(2)	-0.0016(14)	-0.0011(16)	-0.0034(16)
C3	0.024(2)	0.034(2)	0.028(2)	-0.0063(18)	0.0026(18)	-0.011(2)
C4	0.027(2)	0.040(2)	0.019(2)	-0.009(2)	0.0014(17)	-0.0039(19)
C5	0.0186(19)	0.028(2)	0.019(2)	-0.0061(16)	0.0020(16)	-0.0001(17)
C6	0.083(9)	0.083(9)	0.23(3)	0.0000	0.0000	0.0000

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S6. Bond lengths (Å) of **1.**

atom	atom	distance	atom	atom	distance
Br1	Cu2	2.4421(6)	Br1	Cu2[1)]	2.4776(6)
Cu1	S1	2.3071(9)	Cu1	S1[2)]	2.3071(9)
Cu1	S2	2.3017(9)	Cu1	S2[2)]	2.3017(9)
Cu2	S1[3)]	2.3428(10)	Cu2	S2	2.3862(10)
Cl1	C6	1.807(3)	S1	C1	1.741(4)
S2	C1	1.744(3)	N1	C1	1.295(5)
N1	C2	1.486(5)	N1	C5	1.482(5)
C2	C3	1.525(6)	C3	C4	1.526(7)
C4	C5	1.520(6)			

Symmetry Operators:

(1) Y+3/4-1,-X+3/4,Z+3/4-1 (2) -X+1,-Y+1,-Z

(3) Y+3/4-1,-X+1/4+1,-Z+1/4

Table S7. Bond angles (°) of **1.**

atom	atom	atom	angle	atom	atom	atom	angle
Cu2	Br1	Cu2[1)]	118.82(2)	S1	Cu1	S1[2)]	180.00(4)
S1	Cu1	S2	78.28(3)	S1	Cu1	S2[2)]	101.72(3)
S1[2)]	Cu1	S2	101.72(3)	S1[2)]	Cu1	S2[2)]	78.28(3)
S2	Cu1	S2[2)]	180.00(4)	Br1	Cu2	Br1[3)]	112.30(2)
Br1	Cu2	S1[4)]	111.32(3)	Br1	Cu2	S2	113.11(3)
Br1[3)]	Cu2	S1[4)]	111.41(3)	Br1[3)]	Cu2	S2	104.89(3)
S1[4)]	Cu2	S2	103.31(3)	Cu1	S1	Cu2[5)]	115.63(4)
Cu1	S1	C1	84.20(13)	Cu2[5)]	S1	C1	109.03(13)
Cu1	S2	Cu2	107.63(3)	Cu1	S2	C1	84.30(13)
Cu2	S2	C1	102.62(13)	C1	N1	C2	124.5(3)
C1	N1	C5	124.2(3)	C2	N1	C5	111.3(3)
S1	C1	S2	113.2(2)	S1	C1	N1	123.6(2)
S2	C1	N1	123.1(3)	N1	C2	C3	103.4(3)
C2	C3	C4	103.8(3)	C3	C4	C5	103.1(3)
N1	C5	C4	102.7(3)	Cl1	C6	Cl1[6)]	98.57(15)
Cl1	C6	Cl1[7)]	134.58(14)	Cl1	C6	Cl1[8)]	98.57(17)
Cl1[6)]	C6	Cl1[7)]	98.57(17)	Cl1[6)]	C6	Cl1[8)]	134.58(14)
Cl1[7)]	C6	Cl1[8)]	98.57(15)				

Symmetry Operators:

(1) Y+3/4-1,-X+3/4,Z+3/4-1
(2) -X+1,-Y+1,-Z
(3) -Y+3/4,X+1/4,Z+1/4
(4) Y+3/4-1,-X+1/4+1,-Z+1/4
(5) -Y+1/4+1,X+1/4,-Z+1/4
(6) Y+3/4,-X+1/4+1,-Z+1/4
(7) -X+2,-Y+1/2,Z
(8) -Y+1/4+1,X+1/4-1,-Z+1/4