Supplementary Material

Thiosemicarbazonecopper/Halido Systems: Structure and DFT Analysis of the Magnetic Coupling

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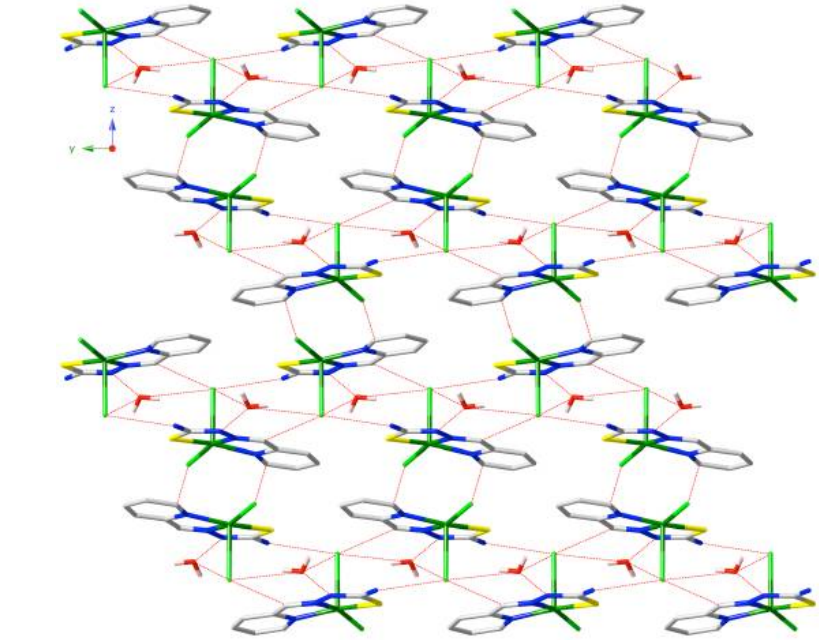
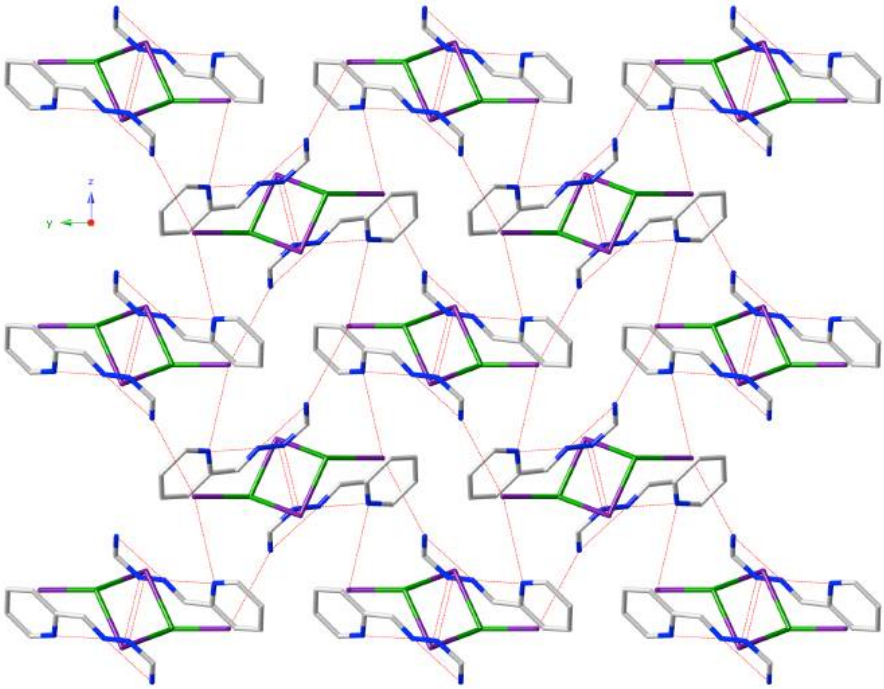
1. Cu/HL/Cl⁻ and Cu/HL/I⁻ compounds

1. Figures

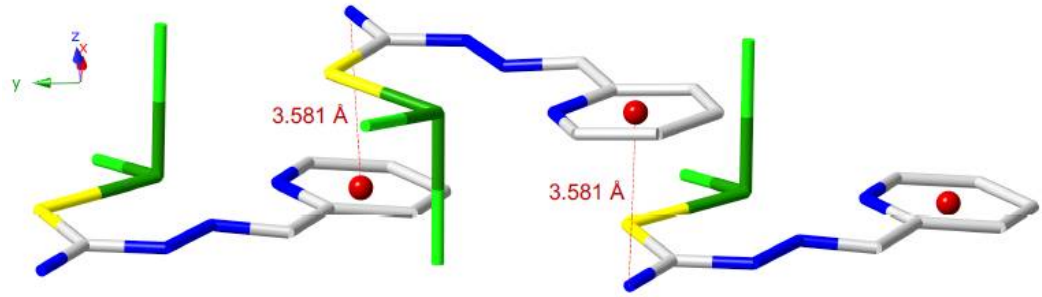


(a)

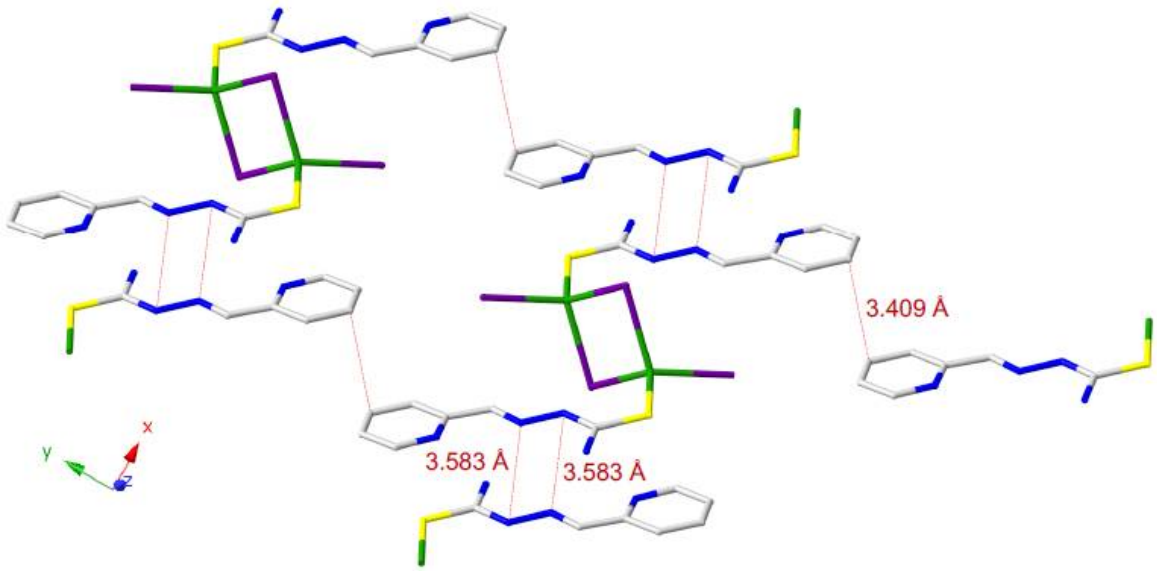


(b)

Figure S1.1. H-bonds (dotted red lines) for compounds ***3*** (a) and **4** (b). Hydrogen atoms (except in water molecules) have been omitted for clarity.

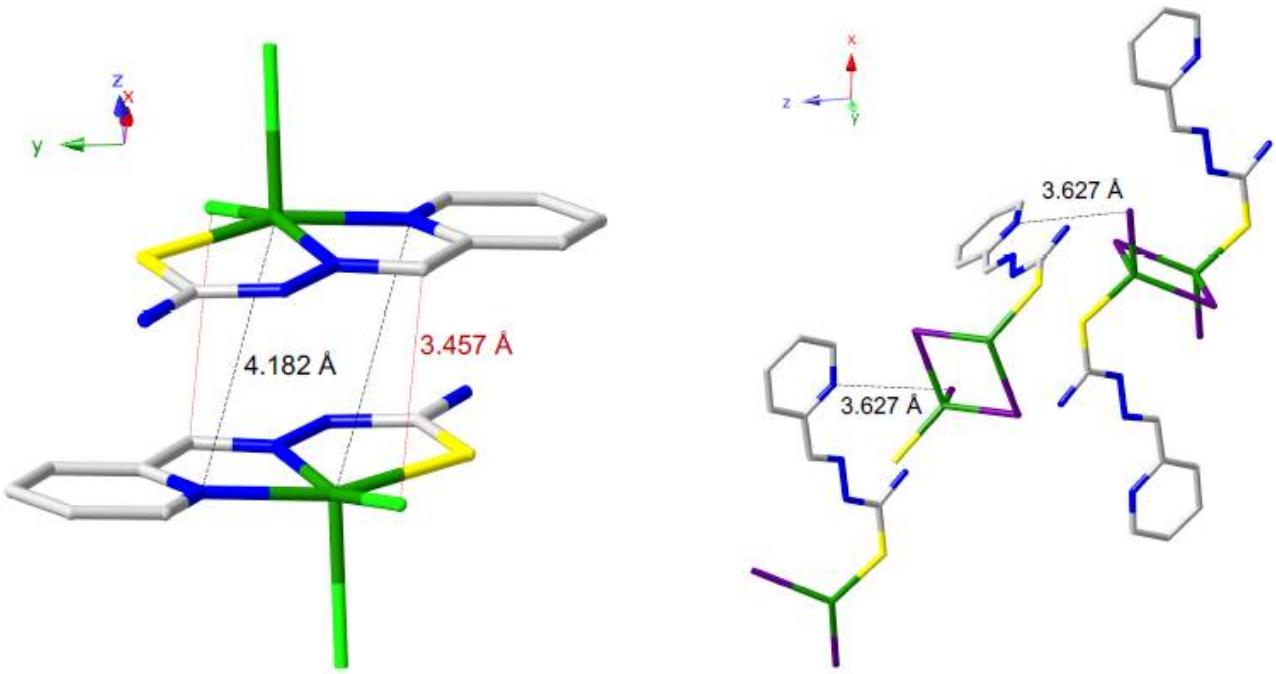


(a)



(b)

Figure S1.2. π–π Stacking interactions for compounds ***3*** (a) and ***4*** (b).



(a) (b)

Figure S1.3. Anion–π interactions for compounds ***3*** (a) and ***4*** (b).

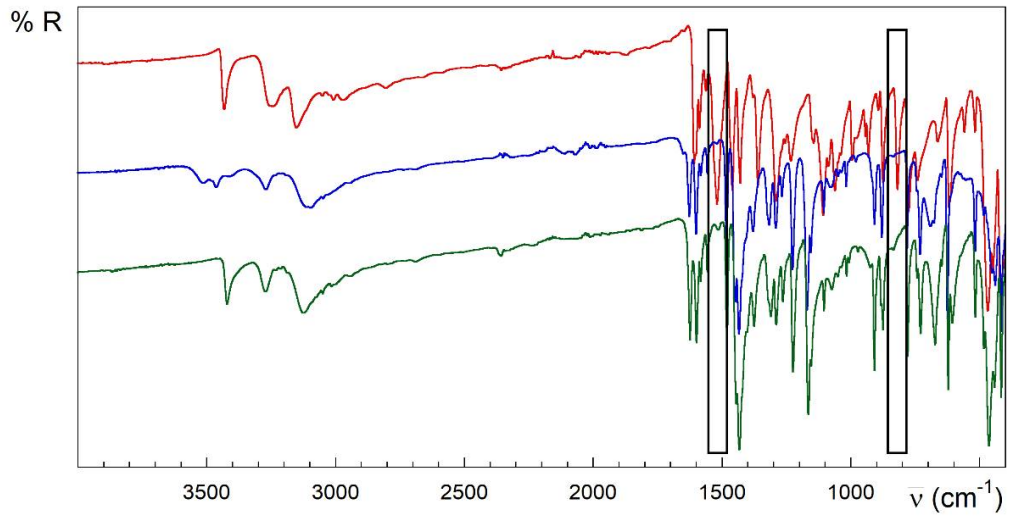


Figure S1.4. FTIR-ATR spectra of HL (red), ***1*** (blue) and ***2*** (green). Rectangles in black highlight the main differences between the spectra of the free ligand and [{CuLX}$_2$] complexes.

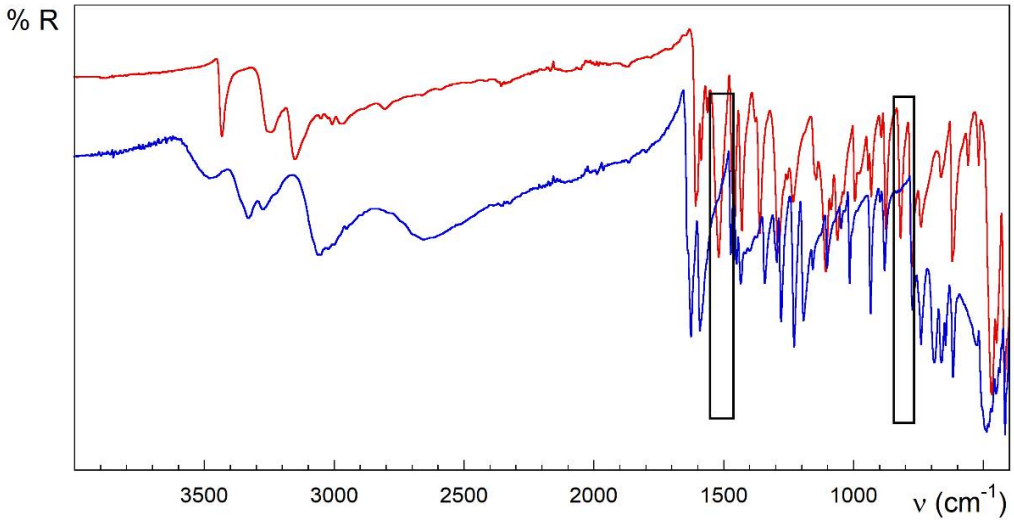


Figure S1.5. FTIR ATR spectra of compounds ***1*** vs ***3***, rectangles frame the A and B regions (see main text).

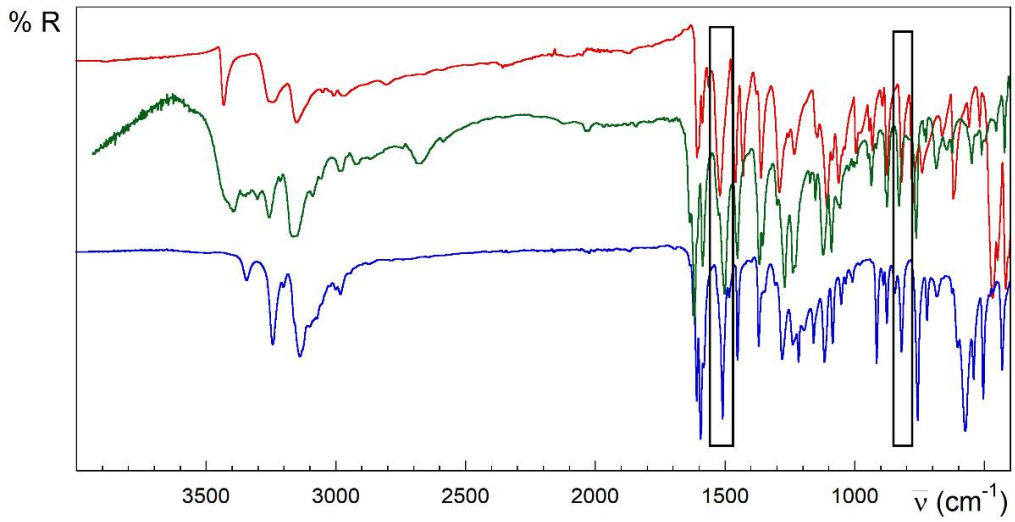


Figure S1.6. FTIR-ATR spectra of HL (red), **$(H_2L)Cl{\cdot}H_2O$** (green) and ***4*** (blue). Rectangles in black show bands in the same spectral regions for the three compounds.

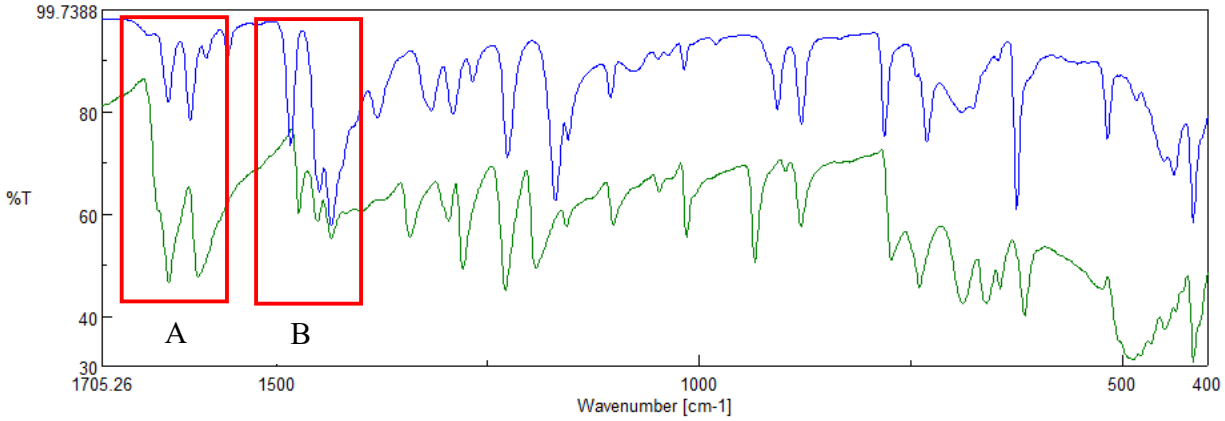
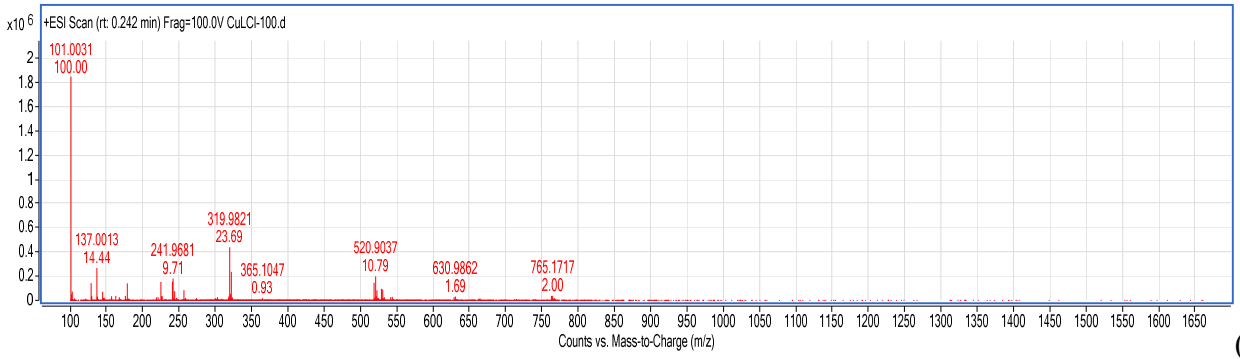
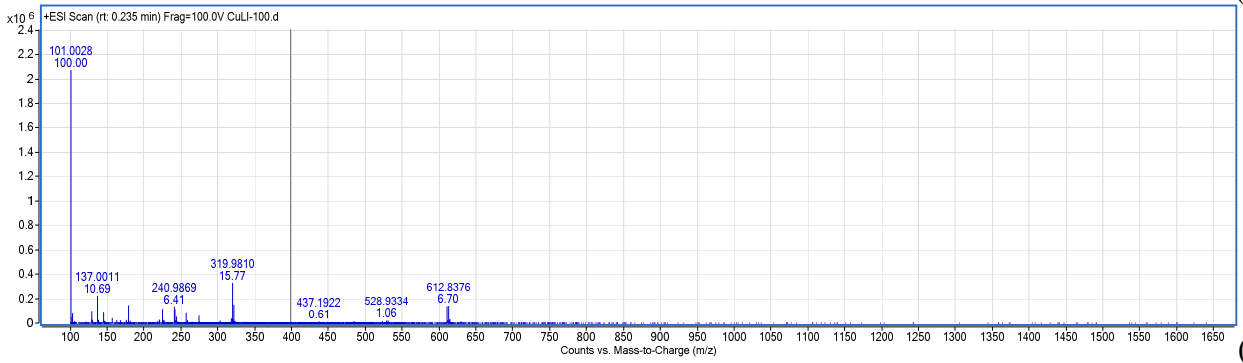


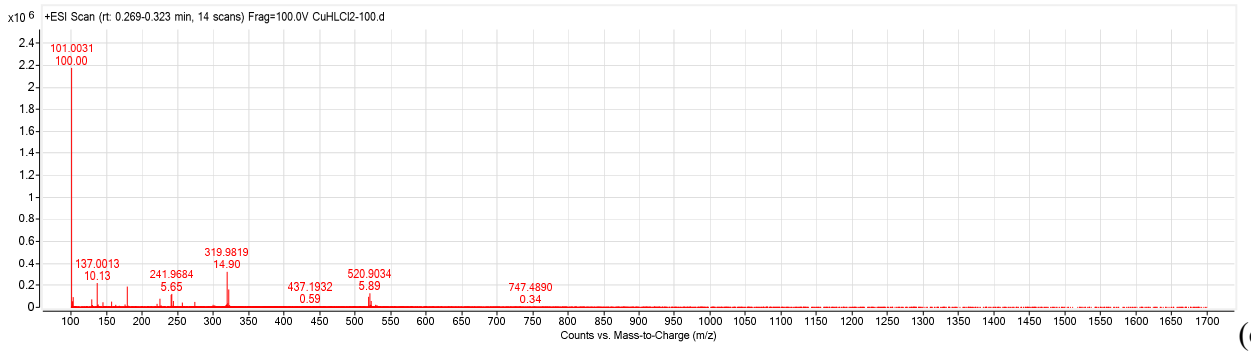
Figure S1.7. FTIR ATR spectra of compounds ***1*** vs ***3***, rectangles frame the A and B regions (see main text).



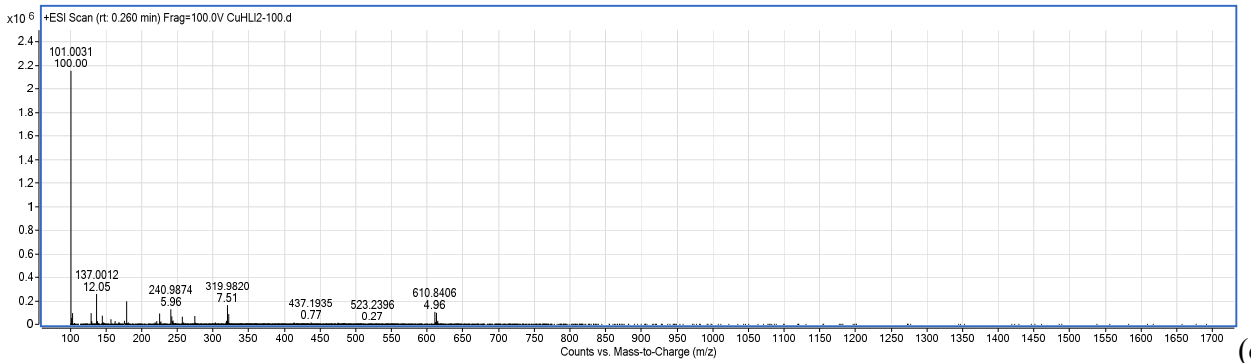
(a)



(b)



(c)



(d)

Figure S1.8. ESI$^+$ mass spectra of compounds ***1*** (a), ***2*** (b), ***3*** (c) and ***4*** (d), in DMSO solution.

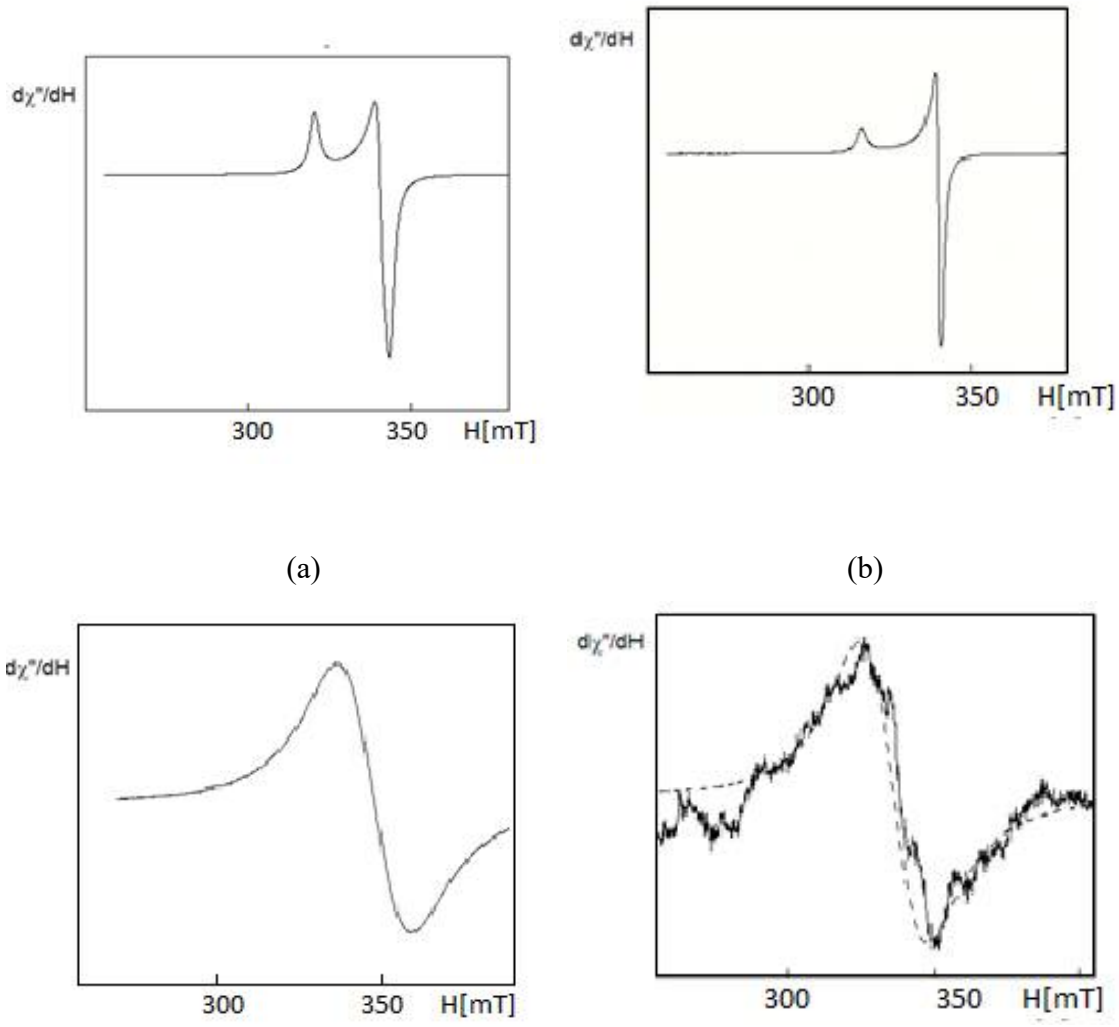


Figure S1.9. X-band EPR spectra at RT of compounds ***1*** (a), ***3*** (b) and ***2*** (c). Impurities in ***4*** (d), whose spectrum has been 120 fold magnified; in dotted lines, the spectrum of ***2*** for comparative purposes.

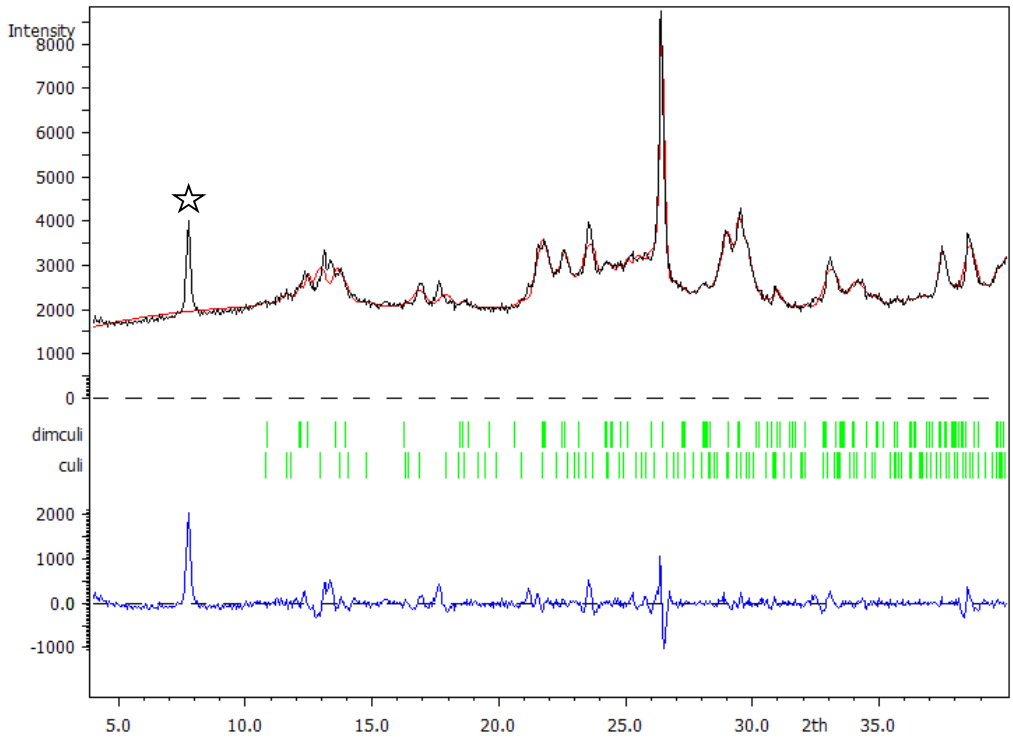


Figure S1.10. XRD pattern experimental (black) and fitted to the calculated diffractograms of compounds ***2*** and ***4*** (red). The only non-fitted peak (marked with a star) corresponds to an unidentified crystalline phase.

2. Tables

Table S1.1. Selected hydrogen bonds (Å, º).

Compound	D–H···A	d (D–H)	d (H···A)	d (D···A)	∠ (DHA)
3	O1W–H1W···Cl2^{i}	0.850	2.55	3.2138(3)	136
	O1W–H2W···Cl2^{ii}	0.850	2.55	3.3580(3)	159
	N3–H3N···O1W^{iii}	0.860	1.85	2.6886(2)	165)
	N4–H42···Cl2^{iii}	0.860	2.31	3.1505(3)	168
	C6–H62···Cl2^{iv}	0.930	2.81	3.6987(3)	159
4	N1–H1A···N2	0.860	2.33	2.686(11)	105
	N1–H1A···I2^{v}	0.860	2.93	3.627(9)	139
	N3–H3N···I1	0.86	2.83	3.616(7)	154
	N4–H4A···N2	0.860	2.31	2.656(11)	104
	N4–H4B···I2^{vi}	0.860	2.84	3.639(8)	155

Symmetry transformations used to generate equivalent atoms: i = –x, y+1/2, –z+1/2; ii = x, y+1, z; ;iii = -x+1, y-1/2, -z+1/2; iv = -x+1, y+1/2, -z+1/2; v = –x+1/2, y+1/2, –z+3/2; vi = x-1/2, -y+1/2, z+1/2.

Table S1.2. Selected IR bands for neutral and anionic thiosemicarbazone derivatives and proposed assignments.

	HL ligand	**Compound 1**	**Compound 2**	**Compound 3**	**Compound 4**
υ(OH)		3514(vw)			
$\upsilon(NH_2)$ + υ(NH)	3433(s)	3462(vw),3409(vw)	3422(s)	3474(w),3341(w),	3344(m),3244(s),
υ(=CH)	3248(m3151(m)	3271(vw),3111(vw)	3273(vw),3130(vw)	3274(vw)	3140(s)
υ(C-H)	3008(vw),2969(vw)			3063-2976(vw)	3072-2982(vw)
$\upsilon(C=N)_{az,py}$ + $\delta(NH_2)$	1608(vs)	1628(s),1602(s)	1626(s),1600(s)	1626(m)	1610(sh, f)
Tioamide I [δ(N-H) + δ(N-H)]	1588(m), 1561(vw)	1582(vw),1557(vw)	1583(vw),1557(vw)	1591(m)	1594(sh, f)
Thioamide I [δ(N-H) + υ(C=N)]	1520(vs)				1509(s)
$Ar(C-C)_{py}$ + $\delta(C-H)_{py}$	1461(vs)	1483(vs)	1481(vs)	1472(vw)	1484(vw)
Thioamide II [δ(N-H) + υ(C=N)]	1430(vs)	1448(m),1436(vs)	1447(m),1436(vs)	1451(vw),1435(vw)	1451(m)
Thioamide III [δ(N-H) + υ(C=N) + δ(N-C-S) + υ(C=S)]	1362(vs),1290(vs), 1233(m),1145(w), 1108(vs),1063(m), 994(vw)	1381(w),1317(w), 1291(w),1268(vw), 1227(s),1171(s), 1155(m),1105(w) 1018(vw),	1376(w),1311(w), 1291(w),1264(vw), 1226(s),1167(s), 1154(m),1105(w) 1017(vw),	1373(vw),1342(w), 1297(w),1280(m), 1229(m),1193(m), 1156(w),1102(w), 1049(vw),1034(vw), 1015(w)	1370(m),1347(w), 1307(vw),1281(m), 1241(w),1217(w), 1197(w),1159(w), 1117(m),1086(w), 1053(w),1035(w), 1010(vw),
υ(N-N)	932(vw)	909(m)	909(m)	934(m)	915(m)
δ(=CH)	876(s)	879(m)	876(sh, m)	880(m)	876(m)
Thioamide IV [υ(C=S)]	820(s)				821(m)
$\gamma(C-C-C/N)_{py}$	775(s),740(m)	781(s),731(sh,m)	780(s),731(sh,m)	772(m),742(m)	758(s),721(m)
(C-C)	619(s)	626(s)	623(s)	617(m)	685(w)
$\delta(C-H)_{py}$	559(vw),519(w)	519(w)	519(w)	526-495(vw)	575(s),542(m)
$\gamma(C-H)_{pi}$ + $\gamma(C-C-C/N)_{py}$	419(m)	417(m)	417(m)	416(w)	432(w)

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, az = azomethinic, py = pyridine ring.

2. Computational studies

1. Thermodynamics

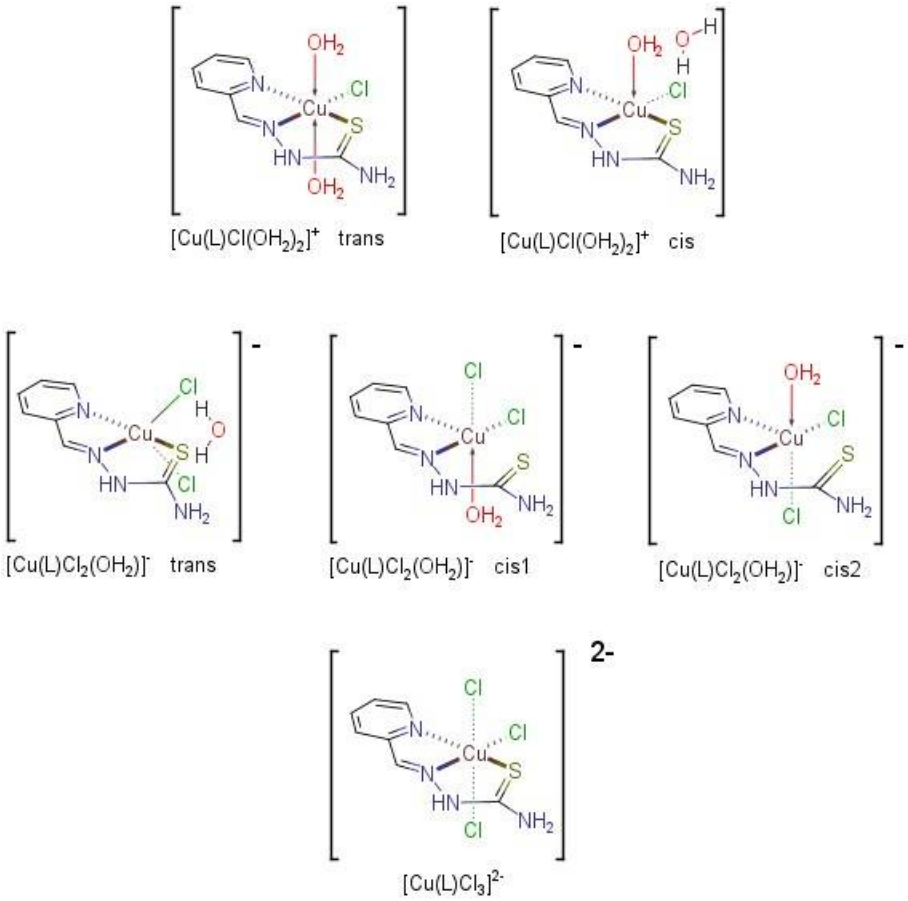


Figure S2.1. Substitution of aqua ligands by chlorido ones in complex with neutral HL ligand.

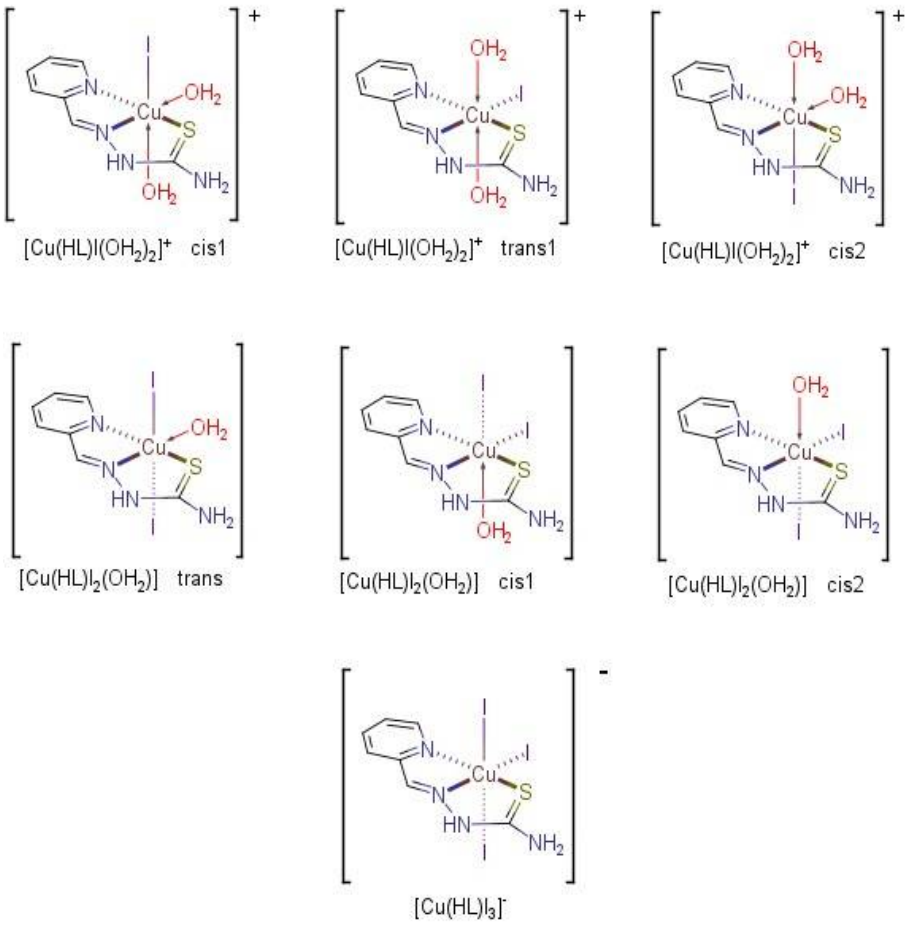


Figure S2.2. Substitution of aqua ligands by iodido ones in complex with neutral HL ligand.

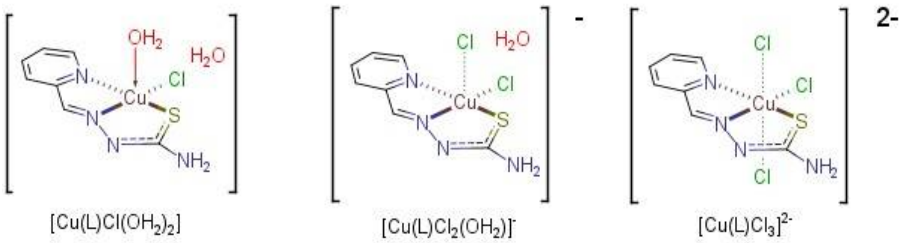


Figure S2.3. Substitution of aqua ligands by chlorido ones in complex with anionic L^- ligand.

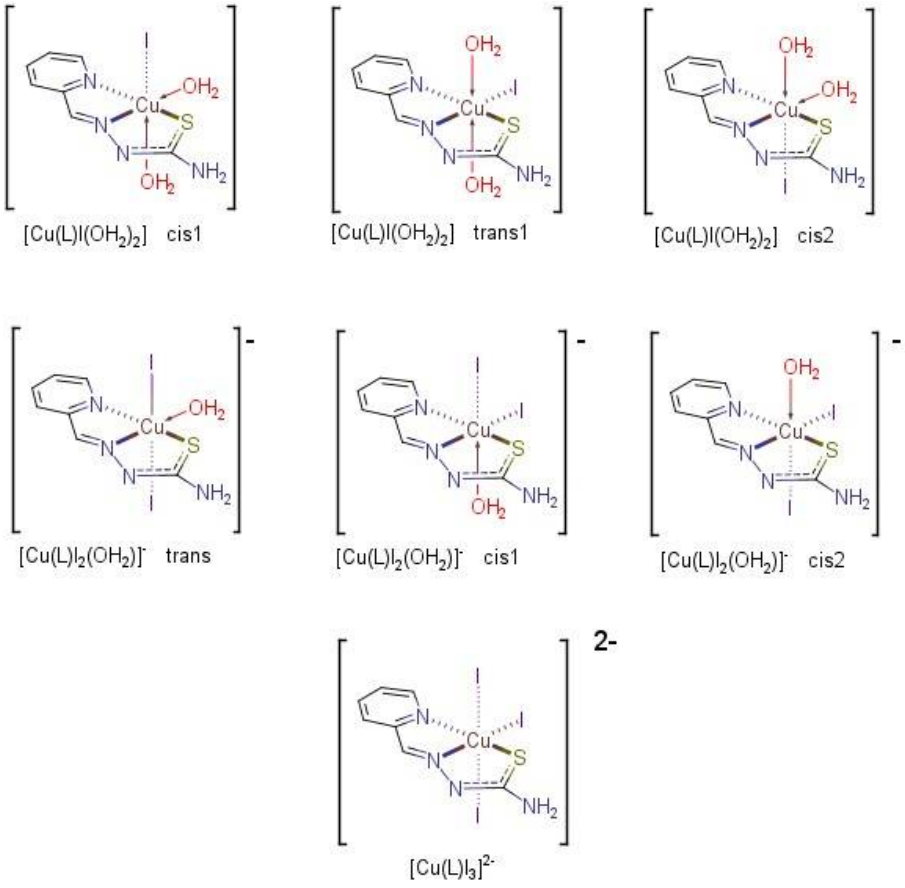


Figure S2.4. Substitution of aqua ligands by iodido ones in complex with anionic L^- ligand.

2. Molecular magnetism

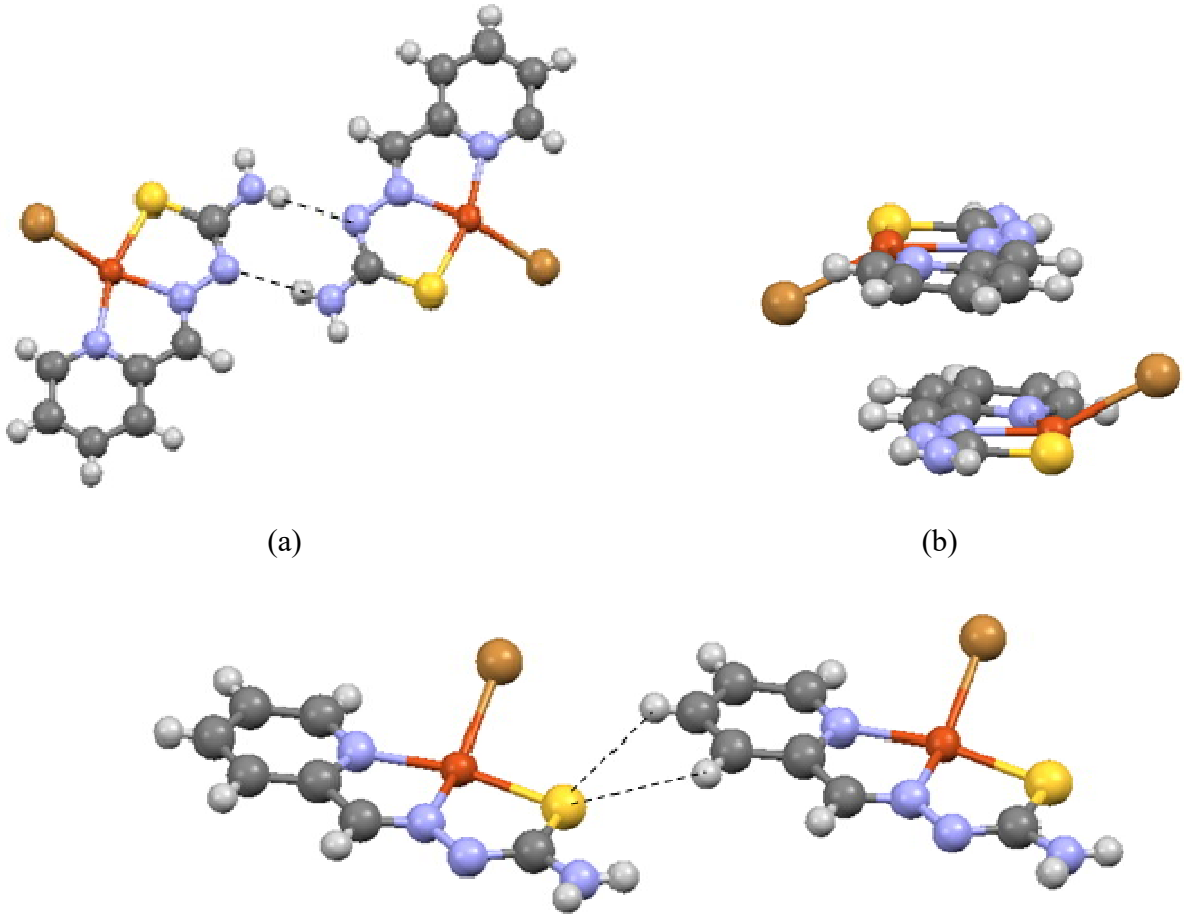


Figure S2.5. Different models to evaluate the intermolecular magnetic interactions in the [{CuLBr}$_2$] compound. (a) Model 1, interaction through the (N···H−N) hydrogen bonds (J_1). (b) Model 2, π−π stacking between two [CuLBr] units (J_2). (c) Model 3, magnetic interactions through (S···H−C) linkages (J_3).

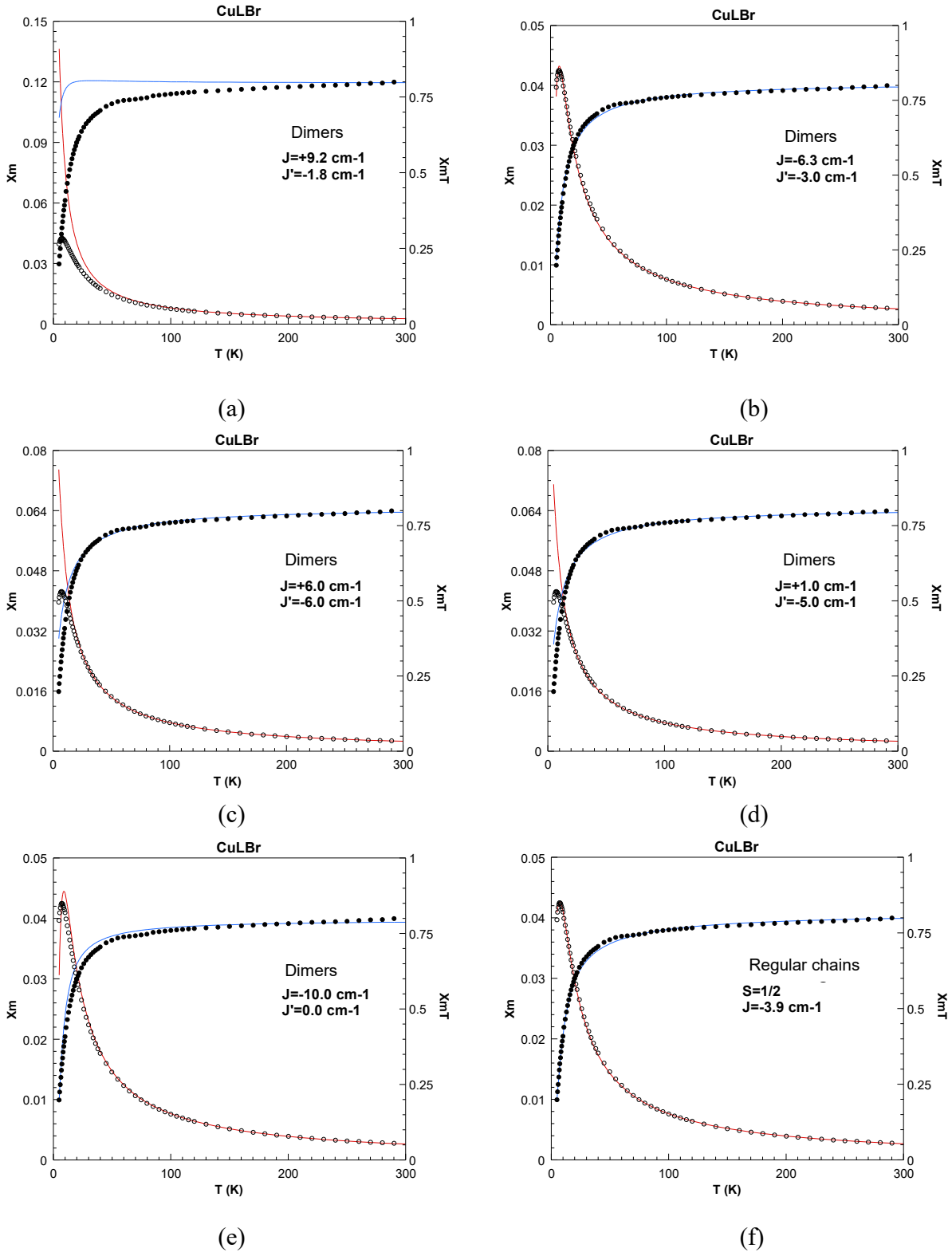


Figure S2.6. Experimental χ_m vs T (●) and χ_mT vs T (○) for the CuLBr (= [{CuLBr}$_2$]) compound, together with the corresponding fits χ_m vs T (red) and χ_mT vs T (blue) considering the J values given on each chart (these values come from a $H = -J\ S_1S_2$ hamiltonian, so that they double those given in text for the J parameter). Note that (c) and (d) are meaningless approaches.