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Supporting Information

Hydrolysis of a carbamate triggered by coordination of metal ions

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Table of contents

1. Crystallographic data of complexes [CuL'$(Cl)_2$] 0.5H_2O 2* and [CdL'$(Cl)_2$] 4*

Coloured crystals of [CuL'$(Cl)_2$] 0.5H_2O **2*** and [CdL'$(Cl)_2$] **4***were obtained as indicated before. The crystals were mounted on a glass fibre and directly used for data collection. Crystal data collection was performed at a 100(2) K temperature using a BRUKER APPEX-II diffractometer with a CCD area detector, using graphite monochromated MoK(α) radiation (λ = 0.71073 Å). Data were treated with APPEX2 software.[1] An empirical absorption correction (SADABS)[2] was applied to the collected reflections. The structure of [CuL'$(Cl)_2$] 0.5H_2O was solved by using the SIR-97 program[3] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 program package.[4] [CdL'$(Cl)_2$] was solved with DIRDIF96 program[5] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 program package.[3] All non-hydrogen atoms were assigned with positional and anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions, riding on attached atoms with isotropic thermal parameters (1.2-1.5 times those of their carrier atoms). Criteria of a satisfactory complete analysis were the ratios of "*rms*" shift to standard deviation less than 0.001 was taken and no significant features were observed in the final difference maps. The molecular graphics include in the manuscript were prepared with MERCURY[6] program. The most relevant crystal data of both crystals are listed below. Important bond distances and angles are summarized in Tables S1 and S2 while hydrogen bond parameters are listed in Tables S3 and S4.

[CuL'$(Cl)_2$] 0.5H_2O 2*: Formula: 2($C_9H_{13}Cl_2CuN_5$)·H_2O; Volume: 2554.1(4) Å^3, MW: 669.38 g·mol^{-1}; Crystal size: 0.32 x 0.17 x 0.03 mm^3; Z= 4; Spatial Group: $P2_1/n$; D: 1.741 mg m^{-3}; Crystal System: Monoclinic; Interval θ: 2.5–23.2 °; a= 16.3718(13) Å; b= 8.9832(7) Å, c= 17.4044(14) Å; α= 90 °; β= 93.781 (4)°; γ= 90 °; μ= 2.12 mm^{-1}; F(000)= 1360; Radiation λ(Mo-K_α) = 0.7107 Å, Measured/unique reflexions: 334364/4637 (Rint= 0.081); R= 0.042; wR= 0.103; GOF= 1.039; Residues: 1.19/-0.69 e Å^{-3}. CCDC: 2174268.

[CdL'$(Cl)_2$] 4*: Formula: $C_9H_{13}CdCl_2N_5$; Volume: 1286.5(5) Å^3, MW: 374.54 g·mol^{-1}; Crystal size: 0.55 x 0.31 x 0.19 mm^3; Z= 4; Spatial Group: $P2_1/n$; D: 1.934 mg m^{-3}; Crystal System: Monoclinic; Interval θ: 2.4-28°; a= 8.366(2) Å; b= 14.446(3) Å, c= 10.650(2) Å; α= 90 °; β= 91.774(4) °; γ= 90 °; μ= 2.10 mm^{-1}; F(000)= 736; Radiation λ(Mo-K_α) = 0.7107 Å, Measured/unique reflexions: 22962/3042 (Rint= 0.032); R= 0.021; wR= 0.054; GOF= 1.093; Residues: 0.36/-0.41 e Å^{-3}. CCDC: 2174283.

Bond Distances (Å)			
Cu(1)-N(1)	1.935(3)	Cu(1B)-N(1B)	1.920(4)
Cu(1)-N(62)	2.038(4)	Cu(1B)-N(62B)	2.047(4)
Cu(1)-N(22)	2.043(4)	Cu(1B)-N(22B)	2.044(4)
Cu(1)-Cl(2)	2.2394(12)	Cu(1B)-Cl(2B)	2.2238(12)
Cu(1)-Cl(3)	2.4925(12)	Cu(1B)-Cl(3B)	2.5394(12)
Bond Angles (°)			
N(1)-Cu(1)-N(62)	78.35(14)	N(1B)-Cu(1B)-N(62B)	78.44(15)
N(1)-Cu(1)-N(22)	78.31(15)	N(1B)-Cu(1B)-N(22B)	79.25(15)
N(62)-Zn(1)-N(22)	154.41(14)	N(62B)-Cu(1B)-N(22B)	155.24(15)
N(1)-Cu(1)-Cl(2)	158.36(11)	N(1B)-Cu(1B)-Cl(2B)	165.62(11)
N(62)-Cu(1)-Cl(2)	97.00(10)	N(62B)-Cu(1B)-Cl(2B)	99.11(11)
N(22)-Cu(1)-Cl(2)	100.83(11)	N(22B)-Cu(1B)-Cl(2B)	99.84(11)
N(1)-Cu(1)-Cl(3)	99.84(11)	N(1B)-Cu(1B)-Cl(3B)	94.44(11)
N(62)-Cu(1)-Cl(3)	99.85(10)	N(62B)-Cu(1B)-Cl(3B)	101.00(11)
N(22)-Cu(1)-Cl(3)	94.34(11)	N(22B)-Cu(1B)-Cl(3B)	91.27(11)
Cl(2)-Cu(1)-Cl(3)	101.78(4)	Cl(2B)-Cu(1B)-Cl(3B)	99.94(4)

Table S1. Main bond distances (Å) and angles (°) in [CuL'$(Cl)_2$] $0.5H_2O$ **2***.

Bond Distances (Å)			
Cd(1)-N(1)	2.2926(17)		
Cd(1)-N(62)	2.3437(19)		
Cd(1)-N(22)	2.4072(18)		
Cd(1)-Cl(2)	2.4264(7)		
Cd(1)-Cl(3)	2.4701(7)		
Bond Angles (°)			
N(1)-Cd(1)-N(62)	69.32(6)	N(22)-Cd(1)-Cl(2)	96.44(5)
N(1)-Cd(1)-N(22)	67.59(6)	N(1)-Cd(1)-Cl(3)	105.25(5)
N(62)-Cd(1)-N(22)	133.70(7)	N(62)-Cd(1)-Cl(3)	98.58(5)
N(1)-Cd(1)-Cl(2)	148.78(4)	N(22)-Cd(1)-Cl(3)	108.23(5)
N(62)-Cd(1)-Cl(2)	112.27(5)	Cl(2)-Cd(1)-Cl(3)	105.23(3)

Table S2. Main bond distances (Å) and angles (°) in [CdL'$(Cl)_2$] **4***.

D-H···A	D···A (Å)	D-H···A (°)	Symmetry Operation
N23—H23*B*···N63*B*^{i}	3.156(6)	139(5)	*x*, *y*+1, *z*
N23—H23*A*···Cl3^{i}	3.248(4)	140(5)	*x*, *y*+1, *z*
N63—H63*B*···Cl3^{ii}	3.180(4)	119(4)	-*x*+1/2, *y*-1/2, -*z*+1/2
N63—H63*A*···Cl2	3.297(4)	129(4)	
N63—H63*B*···Cl2^{ii}	3.460(4)	141(4)	-*x*+1/2, *y*-1/2, -*z*+1/2
N23*B*—H23*D*···Cl2B	3.317(5)	133(4)	
N23*B*—H23*C*···Cl3^{iii}	3.271(4)	150(4)	-*x*+3/2, *y*+1/2, -*z*+1/2
N63*B*—H63*C*···Cl2B	3.337(5)	134(4)	
N63*B*—H63*D*···N63^{ii}	3.069(6)	148(5)	-*x*+1/2, *y*-1/2, -*z*+1/2
O1—H1*O*···Cl3^{iv}	3.489(4)	170(5)	*X*+1/2, −*y*+3/2, *z*+1/2
O1—H2*O*···Cl3B^{i}	3.214(4)	163(6)	*x*, *y*+1, *z*

Table S3. Hydrogen bonds distances (Å) in [CuL'$(Cl)_2$] 0.5H_2O **2*.**

D-H···A	D···A (Å)	D-H···A (°)	Symmetry Operation
N23-H23*A*···Cl2^{i}	3.487(2)	139(3)	*x*+1/2, −*y*+1/2,*z*+1/2
N23-H23*B*···Cl3^{ii}	3.417(3)	141(2)	*x*−1/2, −*y*+1/2,*z*+1/2
N63-H63*B*···Cl3^{iii}	3.250(2)	149(3)	*x*−1/2, −*y*+1/2,*z*−1/2
N63-H63*A*···N23^{iii}	3.034(3)	162(3)	*x*−1/2, −*y*+1/2,*z*−1/2

Table S4. Hydrogen bonds distances (Å) in [CdL'$(Cl)_2$] **4*.**

2. Additional Figures

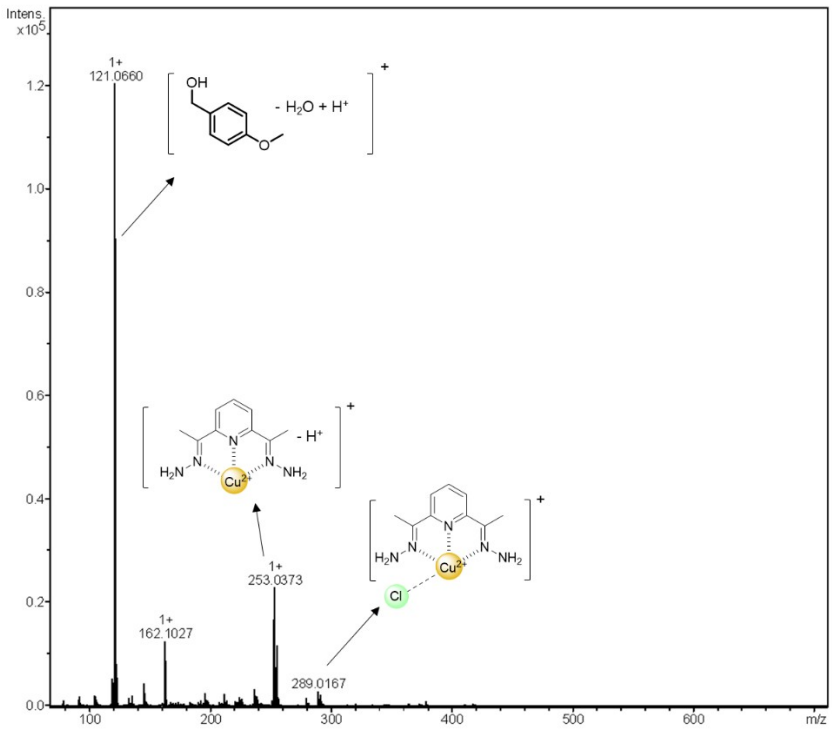

Figure S1. ESI-MS spectrum of organic side-product in the mother liquors of $CuL'(Cl)_2 \cdot H_2O$ **2**.

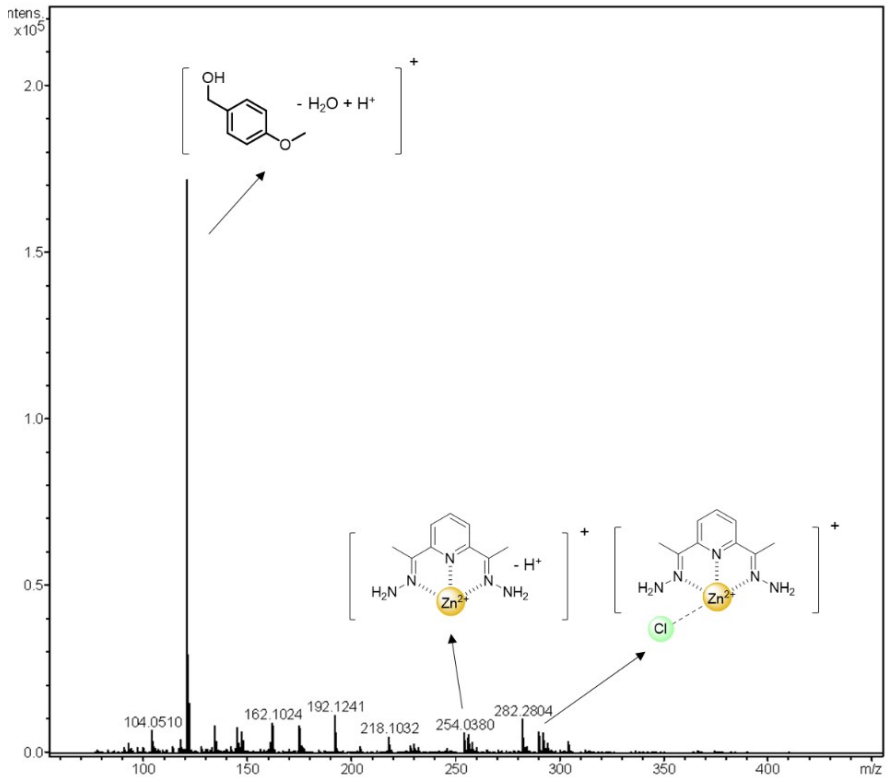

Figure S2. ESI-MS spectrum of organic side-product in the mother liquors of $ZnL'(Cl)_2$ **3**.

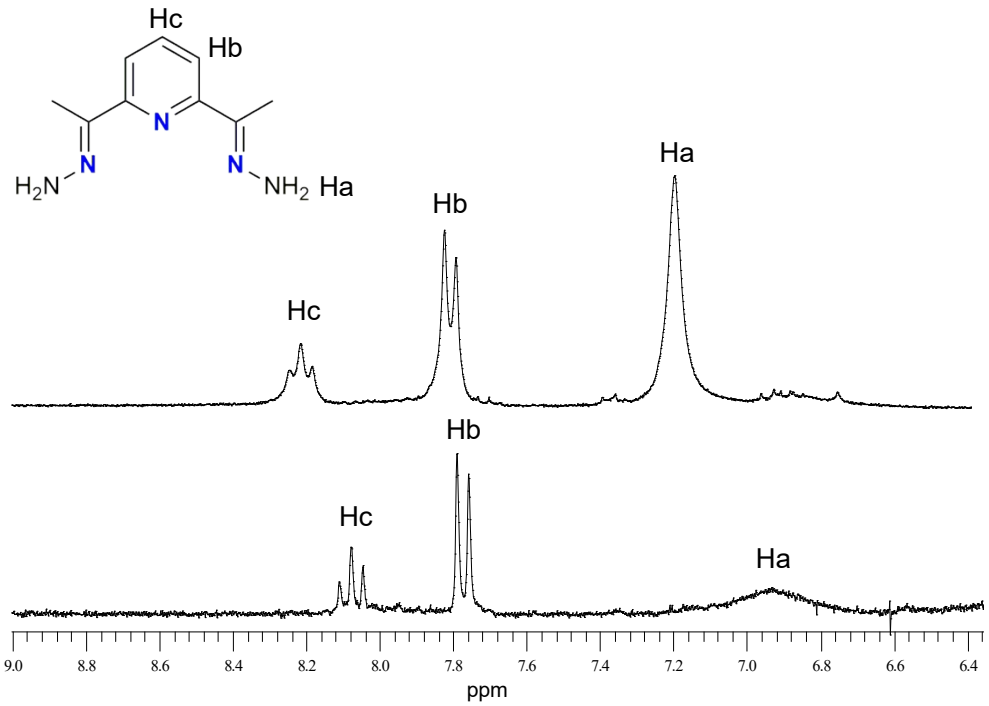

Figure S3. Superposition of ^{1}H NMR spectra of $ZnL'(Cl)_2$ **3** (above) and $CdL'(Cl)_2$ **4** (below) in DMSO-d_6.

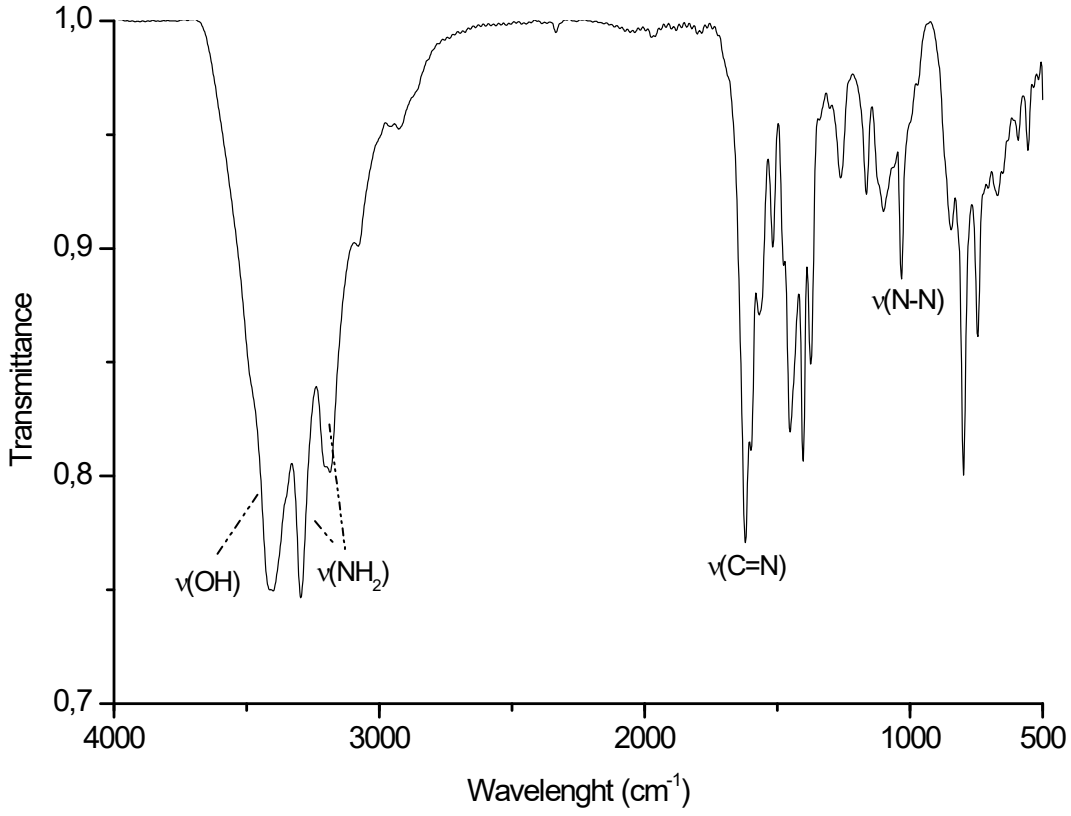

Figure S4. IR spectrum in KBr of the complex $NiL'(Cl)_2 \cdot H_2O$ **1**.

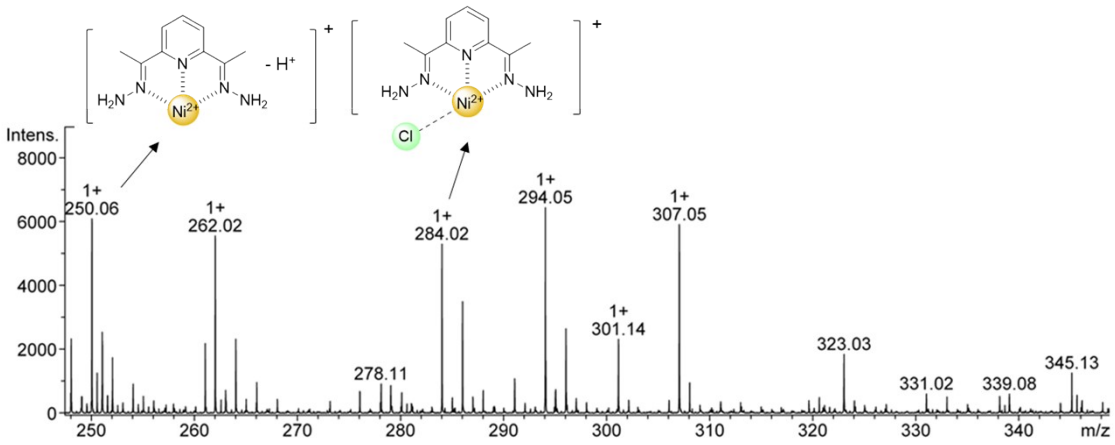

Figure S5. ESI-MS spectrum of the complex NiL´$(Cl)_2 \cdot H_2O$ **1**.

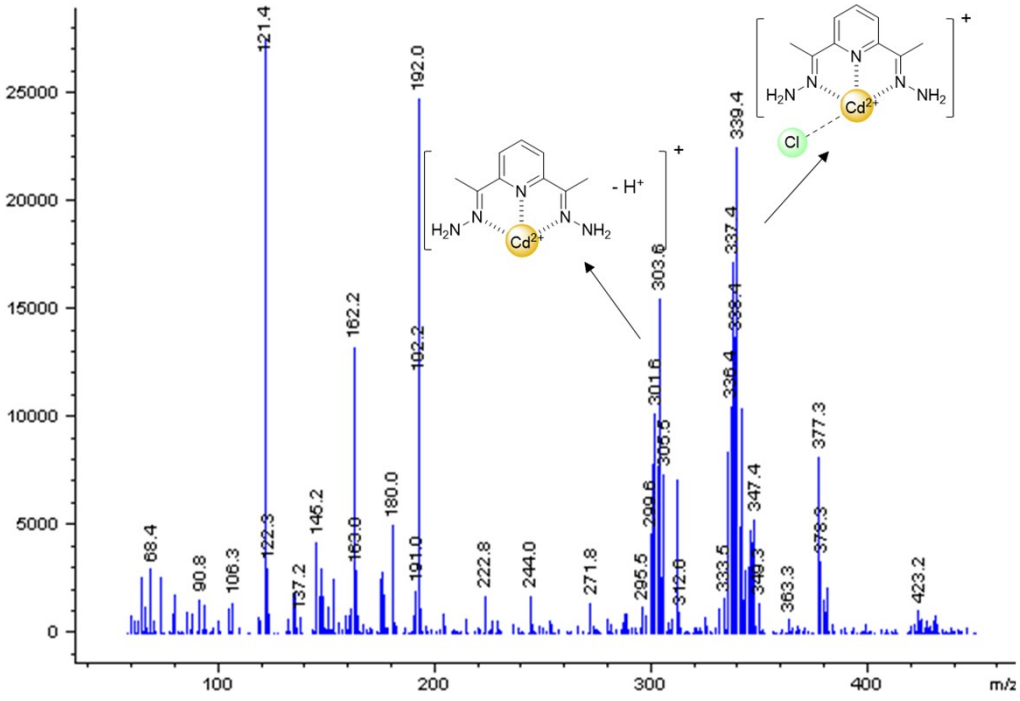

Figure S6. ESI-MS spectrum of the complex CdL´$(Cl)_2$ **4**.

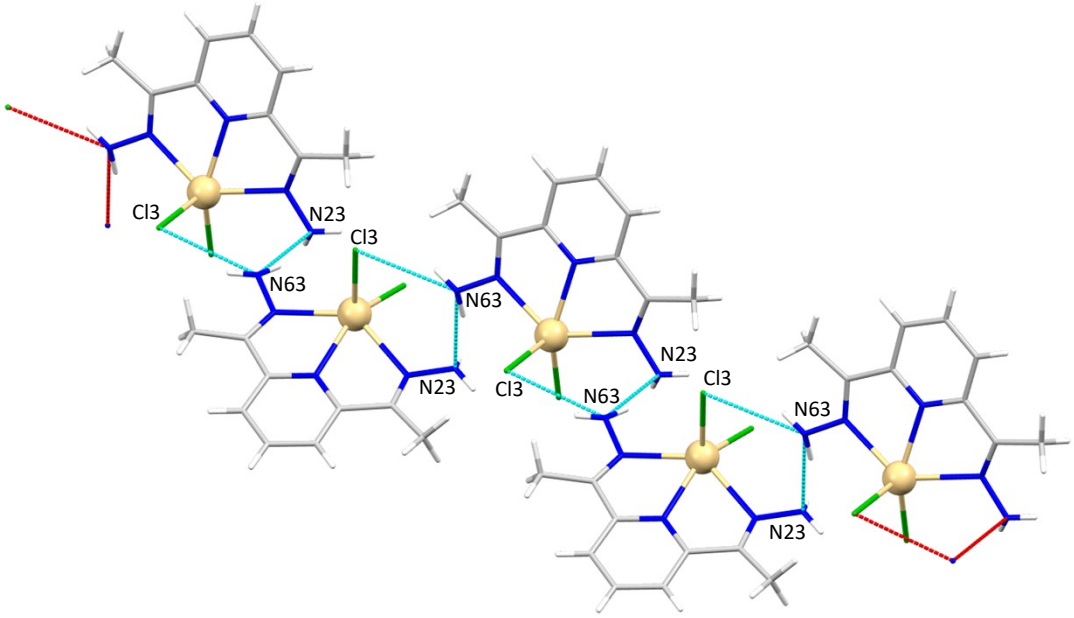

Figure S7. Zigzag arrangement of the molecules of the complex CdL'$(Cl)_2$ **4***forming a 2D network trough hydrogen bonding.

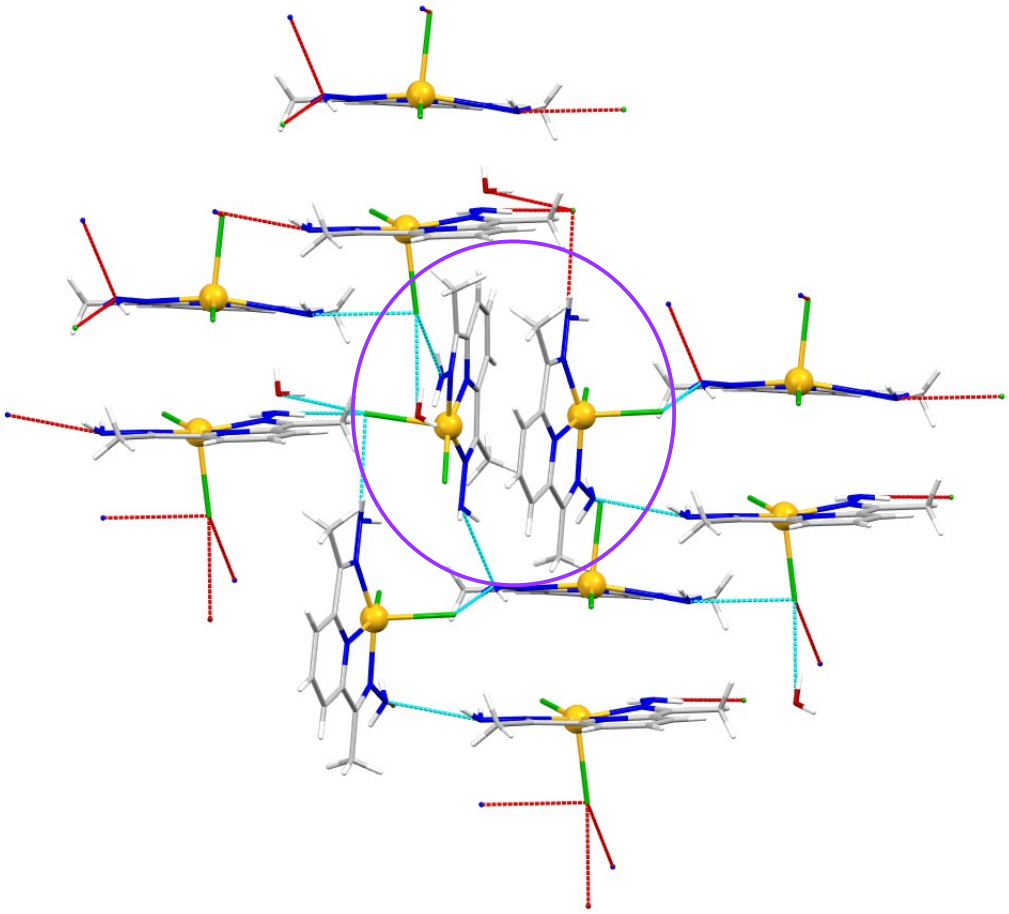

Figure S8. 3D network of the CuL'$(Cl)_2$ $0.5H_2O$ **2*** formed by hydrogen bonding interactions between pairs of "dimers".

3. References

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