Electronic Supplementary Material (ESI) for RSC Advances.

Is Metal Metathesis a Framework-Templating Strategy to Synthesize Coordination Polymers? Transmetallation Studies involving Flexible ligands

Kumari Suman,[a] Fayaz Baig,[a] Rajnikant,[b] Vivek K. Gupta[b] Sanjay Mandal[c] and Madhushree Sarkar*[a]

[a] Department of Chemistry, Birla Institute of Technology and Science , Pilani, Pilani Campus, Rajasthan, India. Fax: +91-1596-244183; Tel: +91-1596-245073; E-mail: msarkar@pilani.bits-pilani.ac.in

[b] Post Graduate Department of Physics, University of Jammu, Jammu Tawi, India. Fax/Tel:+91-191-2432051 E-mail: rkvk.paper11@gmail.com

[c] Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali Mohali (Punjab) 140306, INDIA Email: sanjaymandal@iisermohali.ac.in

Supporting Information

(Synthesis details, ORTEP, IR Spectra, Powder XRD, Atomic Absorption Spectra (AAS), Wavelength Dispersive X-Ray Fluorescence (WD-XRF); Thermogravimetric analysis (TGA)

General: Infra-red spectrum was recorded in FTIR ABB Bomen MB-3000. Elemental analyses were obtained with a Thermo finnigan, Italy, Model FLASH EA 1112 series. Powder X-ray diffraction (XRD) data were recorded with a Rigaku miniflex ll, λ =1.54, Cu Kα. Atomic Absorption Spectra (AAS) was measured using AA-7000, Shimadzu. Wavelength Dispersive X-Ray Fluorescence (WD-XRF) was measured using S8 TIGER, Make: Bruker, Germany; with X-Ray tube of 4KW with 'Rhodium' target and a high volatage/tube current: 60kv/64 mA. Thermogravimetric analysis (TGA) data were recorded under a N_2 atmosphere at a heating rate of 2^oCmin^{-1} with a Perkin-Elmer instrument. The single crystal data was collected on a Xcalibur, Sapphire3 X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω-scan method.[1] The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.[2] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.

Synthesis of ligand 1b: 3-Amino pyridine (2 mmol) was added to 40 mL of a pyridine solution of adipic acid (1 mmol), and the solution was stirred for 15 min. To this solution was added triphenyl phosphite (2 mmol), and the mixture was refluxed for 5 h. The volume of the solution was reduced to 5 mL by distilling out the pyridine, and a white precipitate was obtained. The solid was filtered, washed with water, and dried under vacuum. Yield: 70%. Mp: 216-220°C. FTIR (KBr, cm^{-1}): 3301(w), 3247(m), 3178(m), 3108(m), 3039(m), 2947(vs), 2917(s), 2875(m), 1690(vs), 1580(vs), 1550(s), 1478(m), 1419(vs), 1378(m), 1281(vs), 1157(s), 1132(w), 1034(m), 943(m), 910(w), 856(w), 810(s), 735(w), 701(m), 625(w), 578(w).

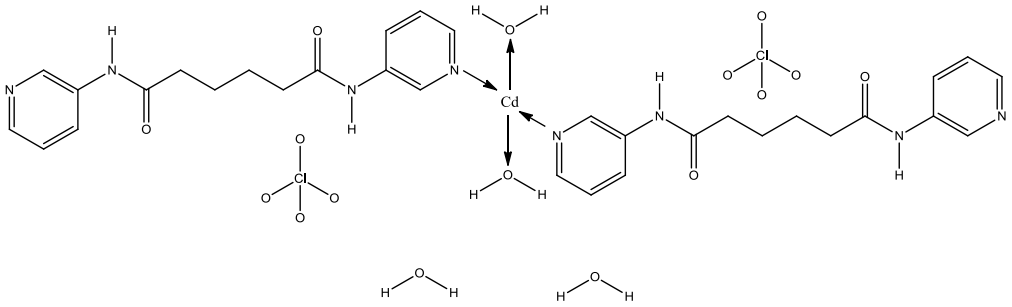
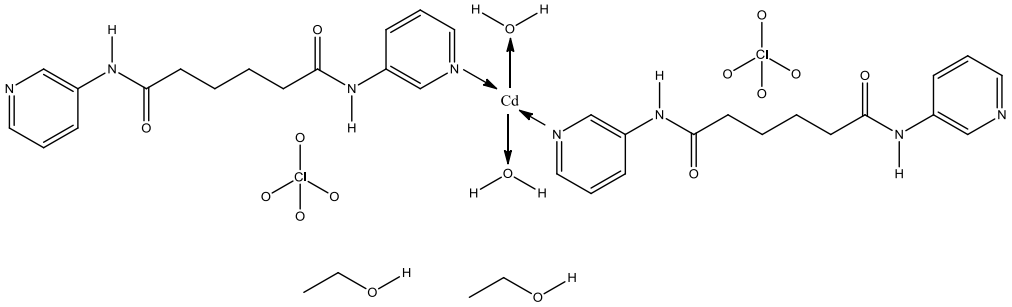
Synthesis of CP-3-Cu, $\{(Cu(\mathbf{1b})_2(H_2O)_2)\bullet 2(ClO_4)\bullet(H_2O)\}_n$:The ligand **1b** (596 mg, 2.0 mmol) dissolved in 15ml of 1:1 mixture of water-Ethanol solvent system. To the above solution, 10 ml ethanolic solution of $Cu(ClO_4)_2.6H_2O$ (370.1 mg, 1.0 mmol) was added. The resulted blue precipitate was dissolved by adding few drops of water. The solution was filtered and kept for slow evaporation. Blue-colored crystals were formed after 8-10 days in 80% yield. Anal. Calcd (%)for $C_{32}H_{44}CuCl_2N_8O_{16}$:C, 41.27; H, 4.72; N 12.03 Found: C, 41.27; H, 4.55; N, 11.63; FTIR (KBr, cm^{-1}): 3564(s), 3278(s), 3201 (w), 3101(w), 2931(w), 2862(w), 1674(s), 1612(w), 1589(w), 1550(vs), 1488(m), 1427(s), 1365(w), 1296 (m), 1242(w), 1195(w), 1103(vs), 956(w), 918(w), 810(m), 702(m), 624(m), 555(w).

Synthesis of CP-4-Cd, $\{(Cd(\mathbf{1b})_2(H_2O)_2)\bullet 2(ClO_4)\bullet 2(H_2O)\}_n$: Microwave assisted technique was used wherein ligand **1b** (59.6 mg, 0.2 mmol) and $Cd(ClO_4)_2.6H_2O$ (41.94 mg, 0.1 mmol) was taken 5ml of 1:1

mixture of water-Ethanol into a specially designed microwave test tube. The reaction mixture was irradiated for 10 minutes at 90℃, at medium stirring rate and 100 psi pressure. White crystals suitable for single crystal XRD were formed after keeping the solution for a day. Anal. Calcd (%)for $C_{32}H_{44}CdCl_2N_8O_{16}$: C, 39.22; H, 4.53; N, 11.43 Found: C, 41.69; H, 4.57; N, 10.69

FTIR (KBr, cm^{-1}): 3865(s),3841(s), 3741(vs), 3672(m), 3649(m), 3618(m), 3564(w), 3317(vs), 1674(vs), 1527(vs), 1481(s), 1419(s), 1326(w), 1288(m), 1164(w), 1103(vs), 956(w), 802(w), 771(s), 702(w), 624(m), 563(m).

Table S1: Elemental Analysis (Calculated)

Found	C % 41.69	H % 4.57	N % 10.69
Calculated: Chemical Formula: $C_{32}H_{44}CdCl_2N_8O_{16}$ 	C % 39.22	H % 4.53	N % 11.43
Calculated: Chemical Formula: $C_{36}H_{52}CdCl_2N_8O_{16}$ 	C % 41.73	H % 5.06	N % 10.81

Synthesis of CP-4-Cu: Metal-metathesis reaction was performed on **CP-4-Cd** wherein crystals of **CP-4-Cd** were immersed into 0.1 M ethanolic solution of $Cu(ClO_4)_2.6H_2O$. The white crystals slowly turned blue crystals. The crystals were analyzed by IR, Powder XRD, AAS and WD-XRF spectroscopy.

Figure S1. IR spectra of Ligand 1b:

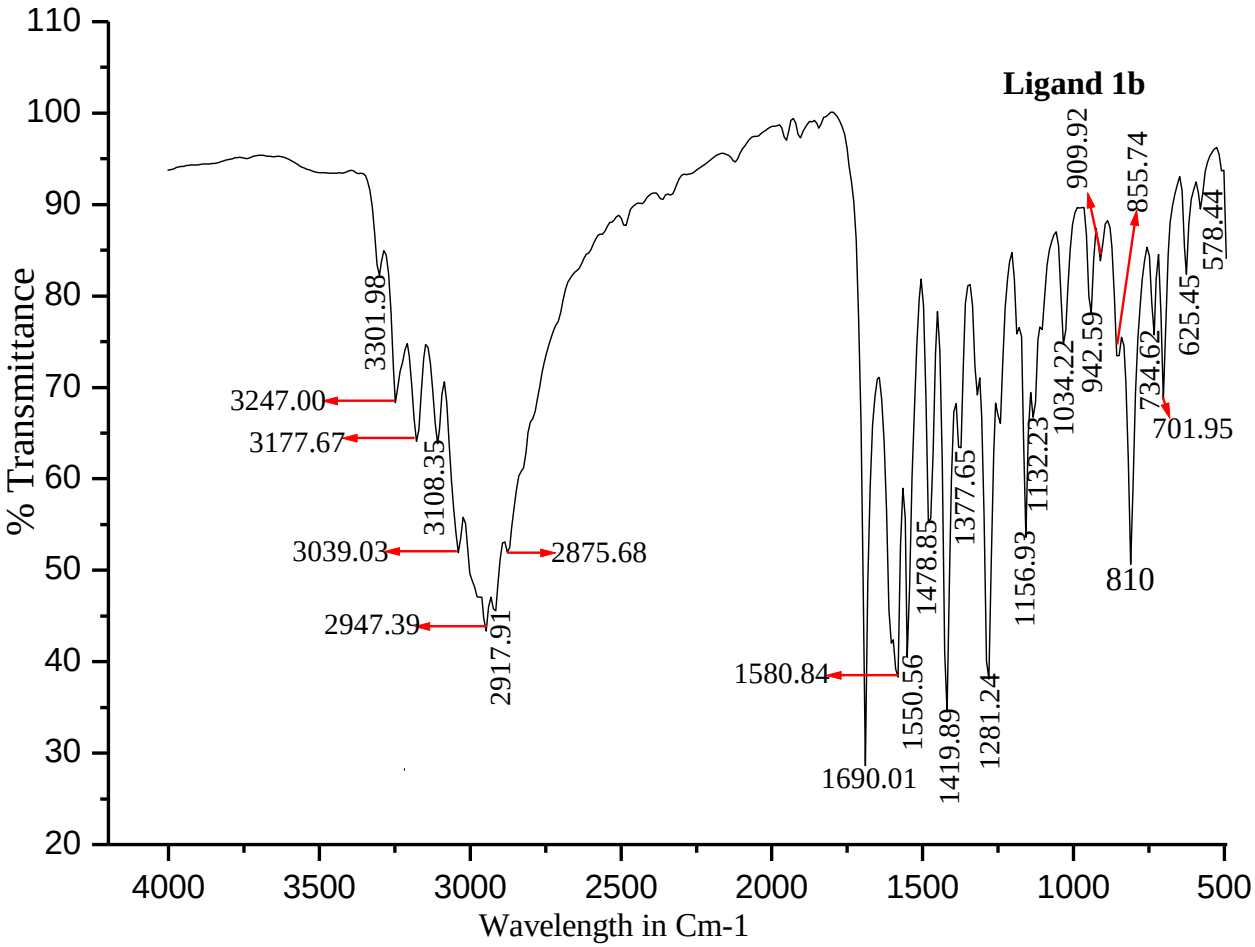


Figure S2. IR Spectra of CP-3-Cu

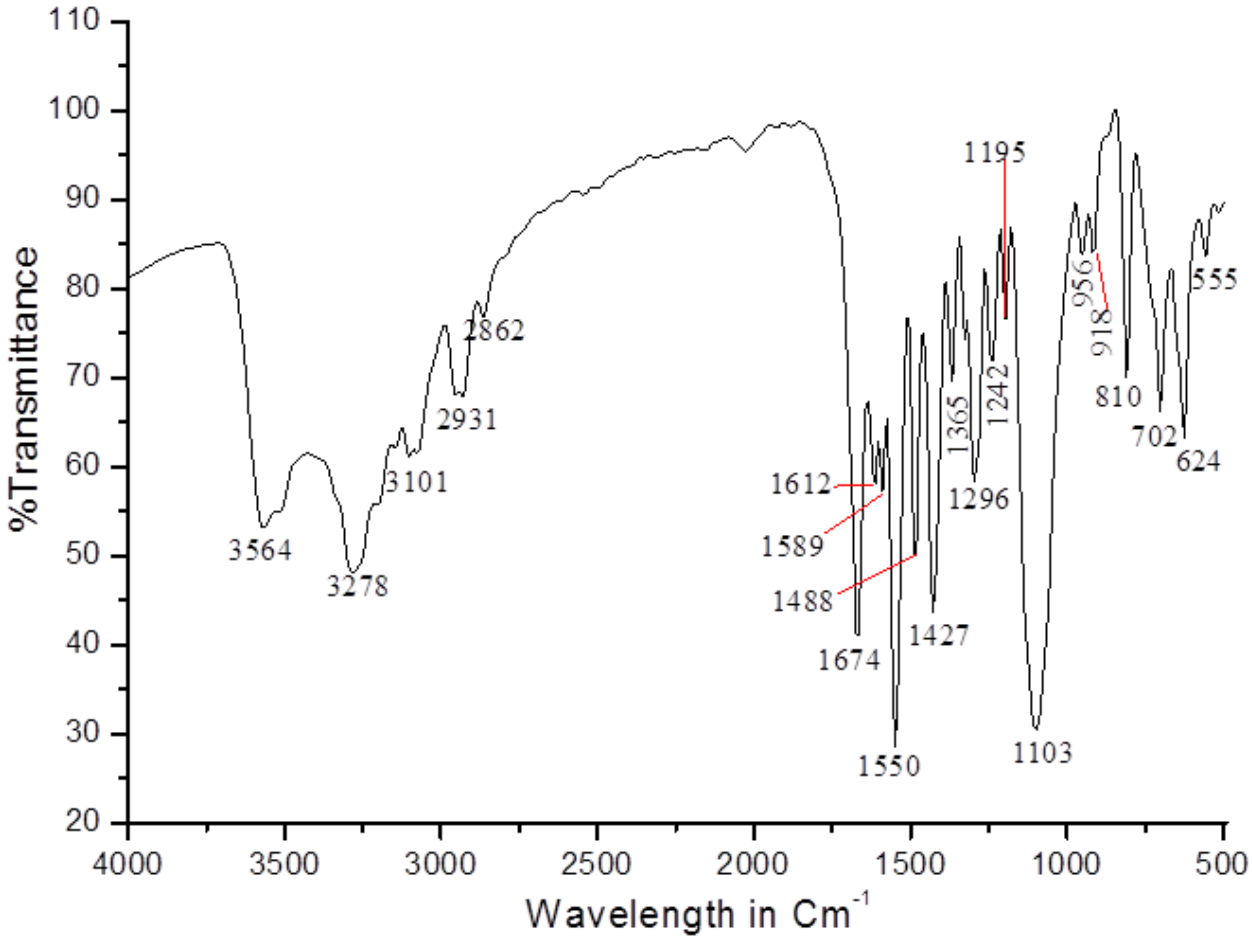


Figure S3. IR Spectra of CP-4-Cd

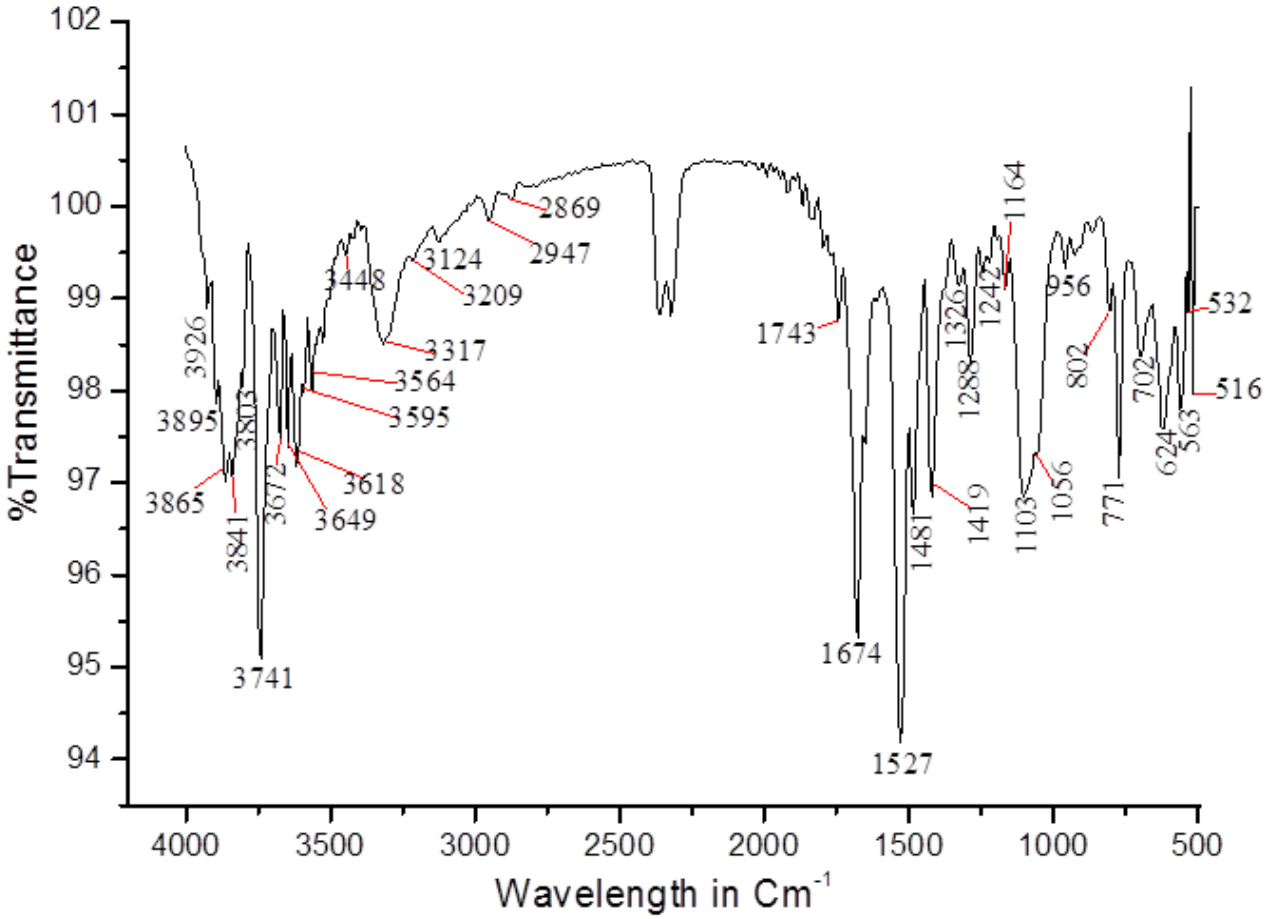


Figure S4. Powder XRD of CP-3-Cu (Calculated)

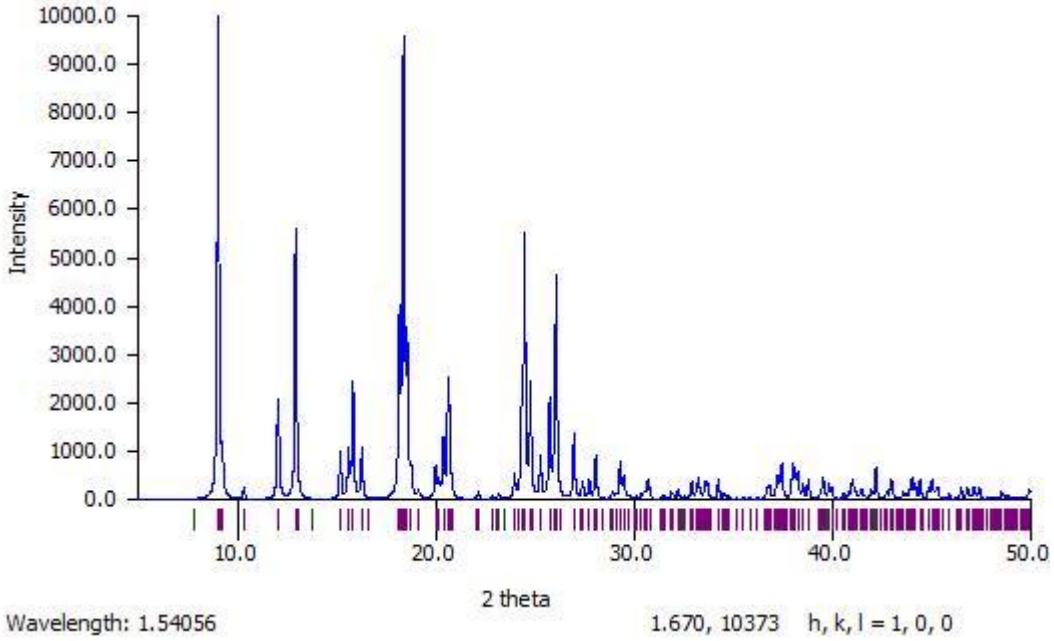


Figure S5: Powder XRD of CP-3-Cu (Experimental)

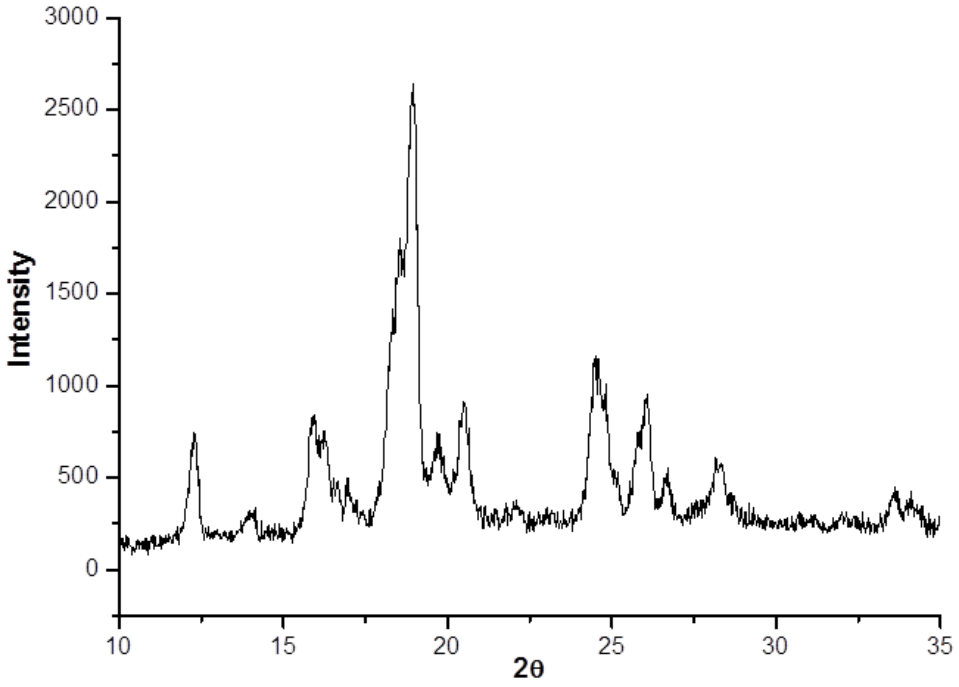


Figure S6. Powder XRD of CP-4-Cd (Calculated)

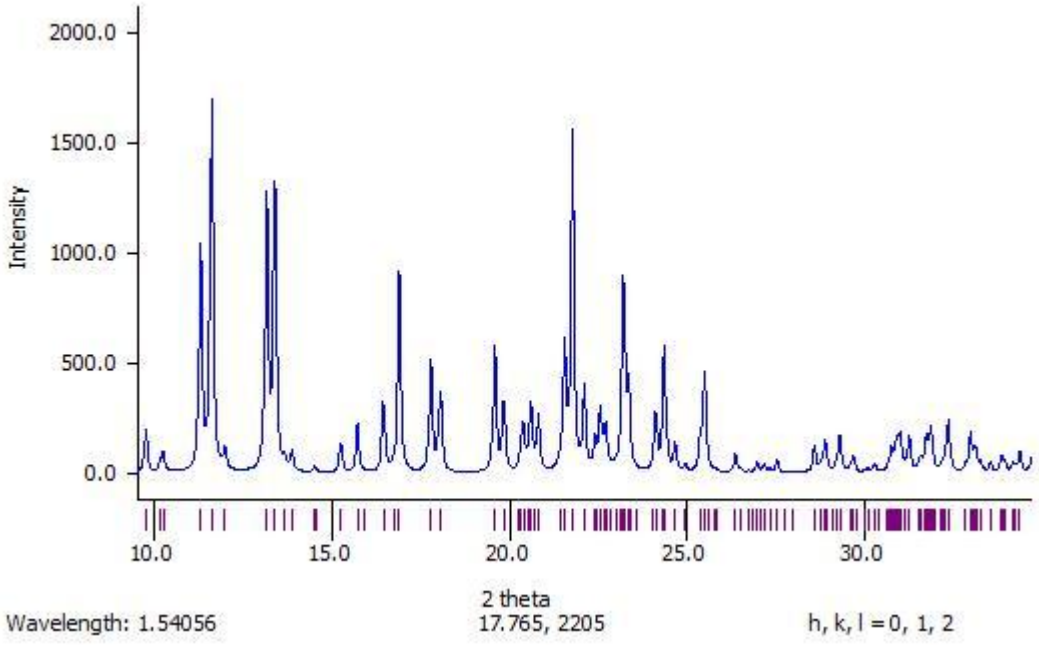


Figure S7: Powder XRD of CP-4-Cd (Experimental)

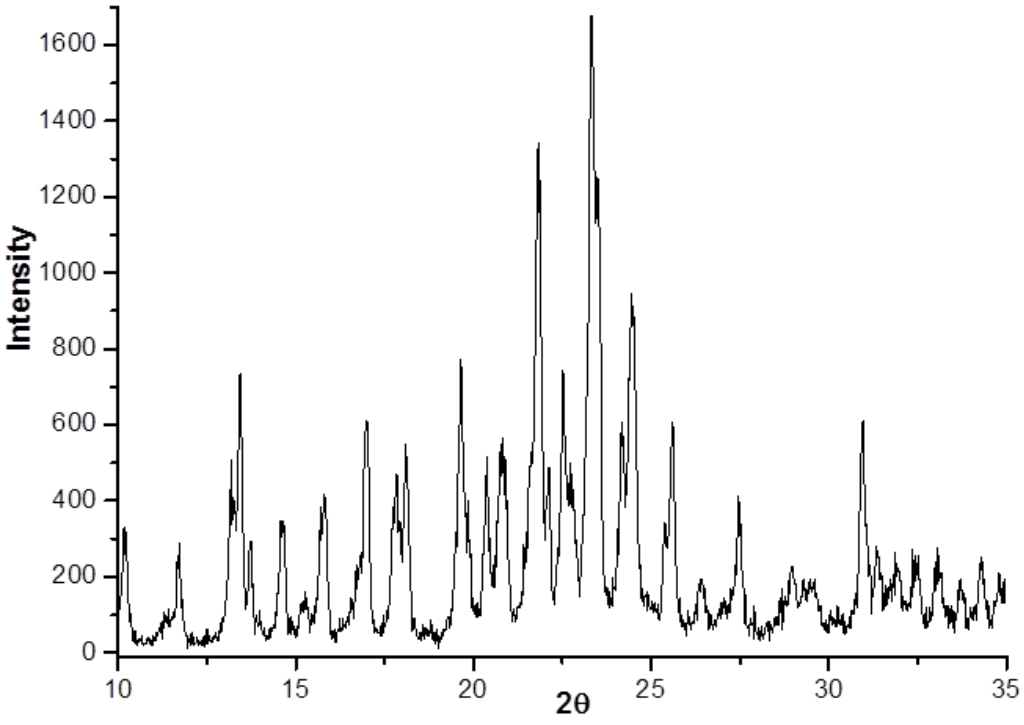


Figure S8: Powder XRD of CP-4-Cu (Experimental)

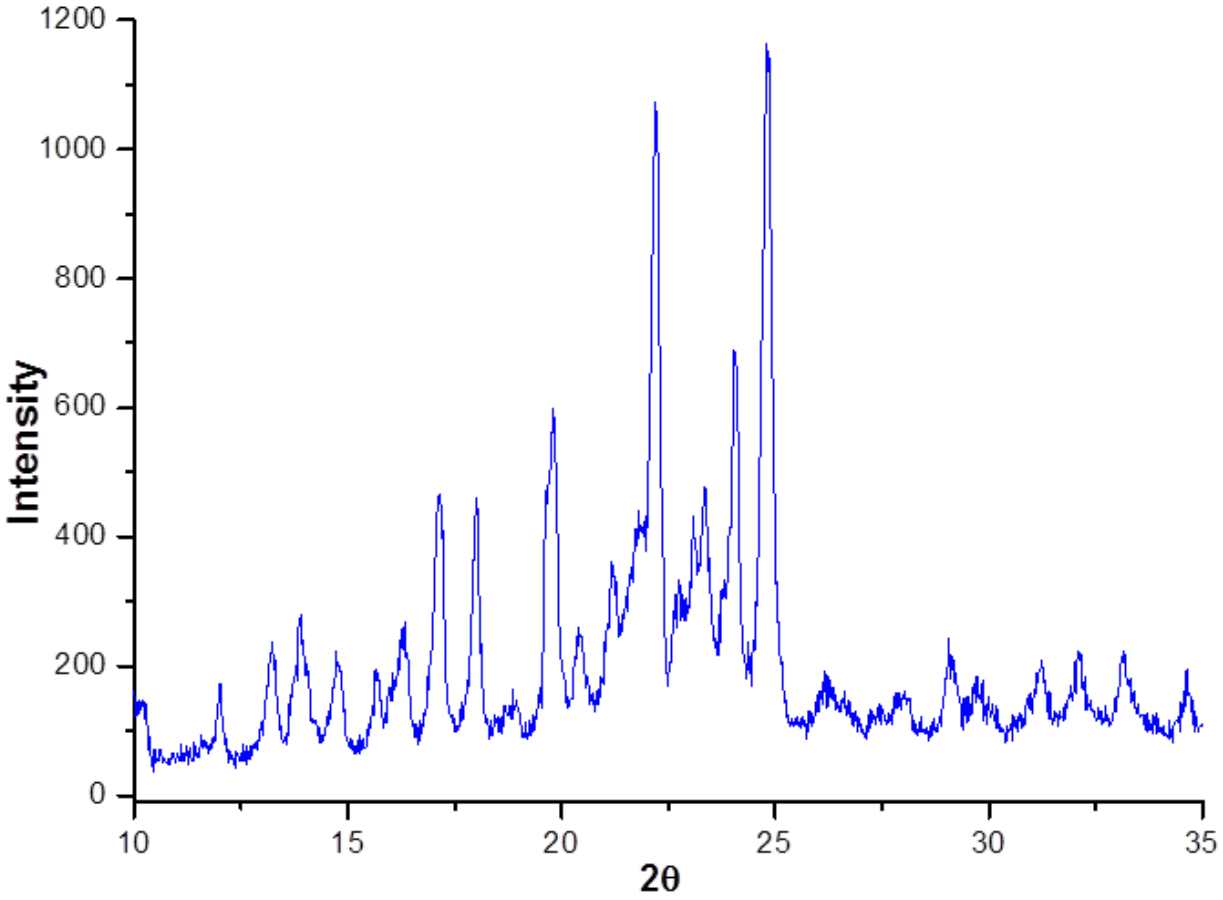


Figure S9: Powder XRD of CP-3-Cu and CP-4-Cu;

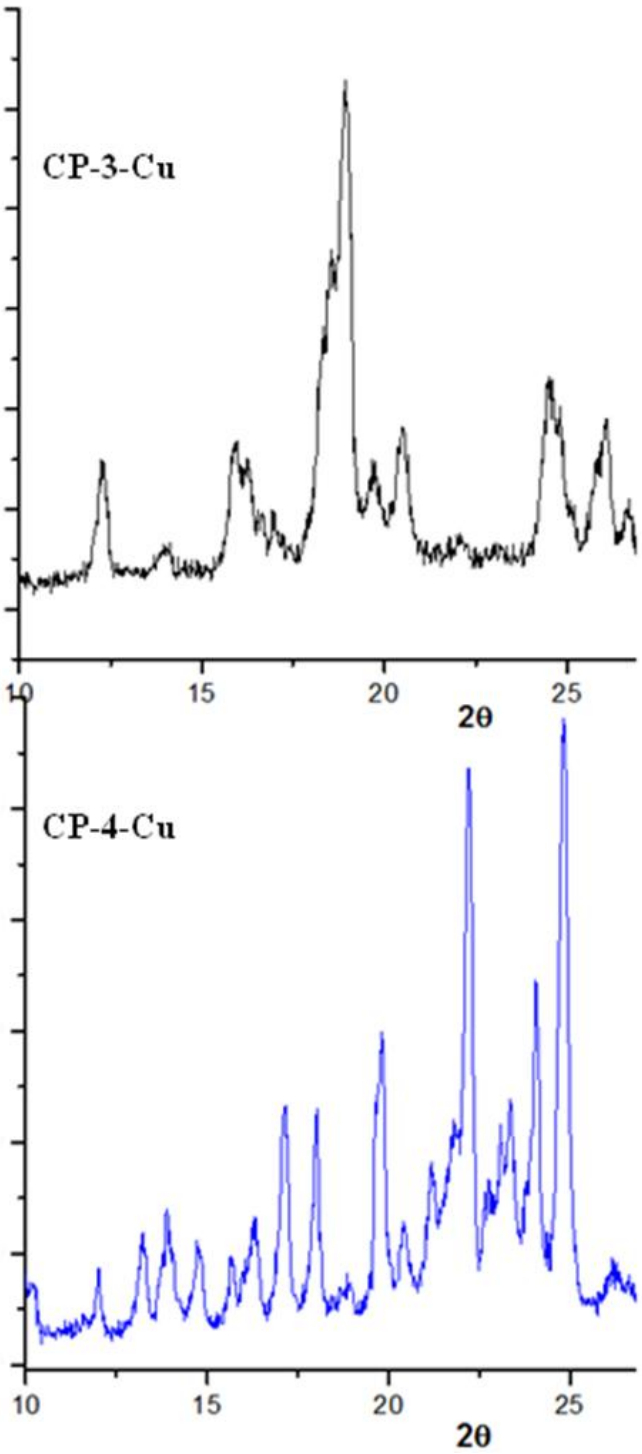
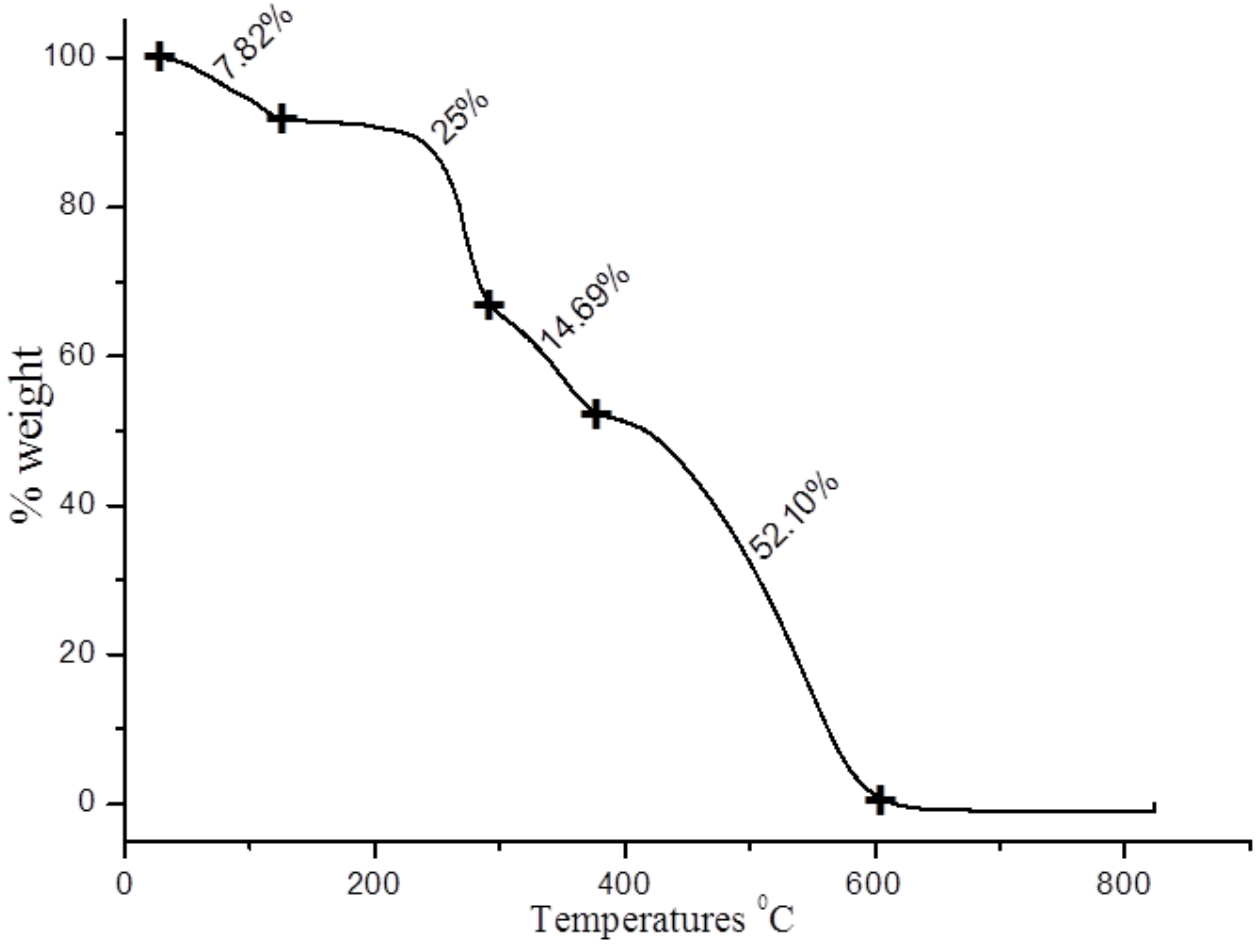
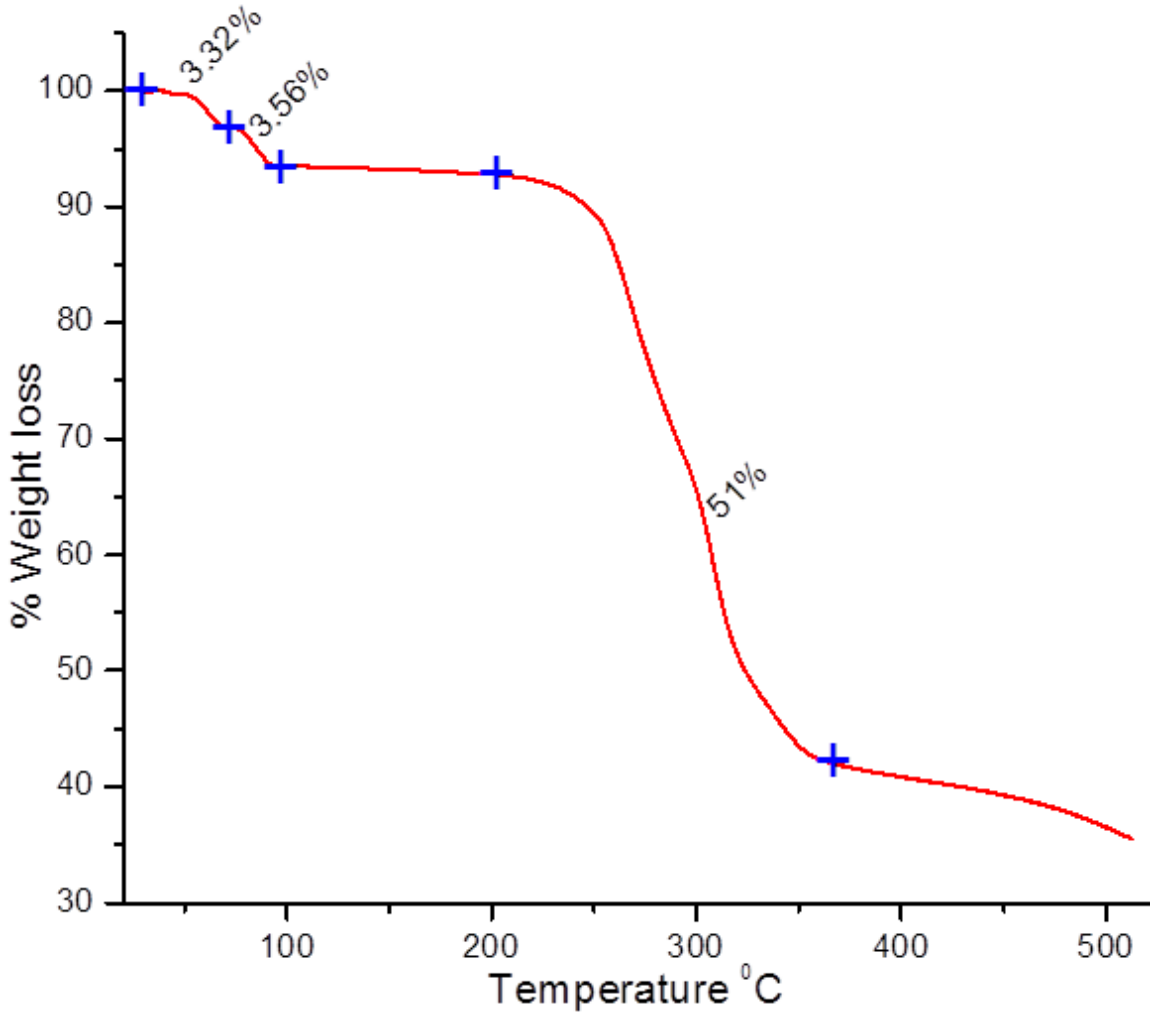


Figure S 10: Thermal Analysis of CP-3-Cu



Initial Weight loss of 7.82 % corresponds to the loss of four water molecules (Calculated 7.804%). The coordination polymer degrades beyond 250°C.

Figure S 11: Thermal Analysis of CP-4-Cd



Initial Weight loss of 3.32 % corresponds to the loss of two water molecules (Calculated 3.70%). The weight loss of 3.56% corresponds to the further loss of two water molecules (Calculated 3.84%)..

Figure S 12: WD-XRF of the Transmetallation Reaction at various intervals (Intensity *vs* 2θ)

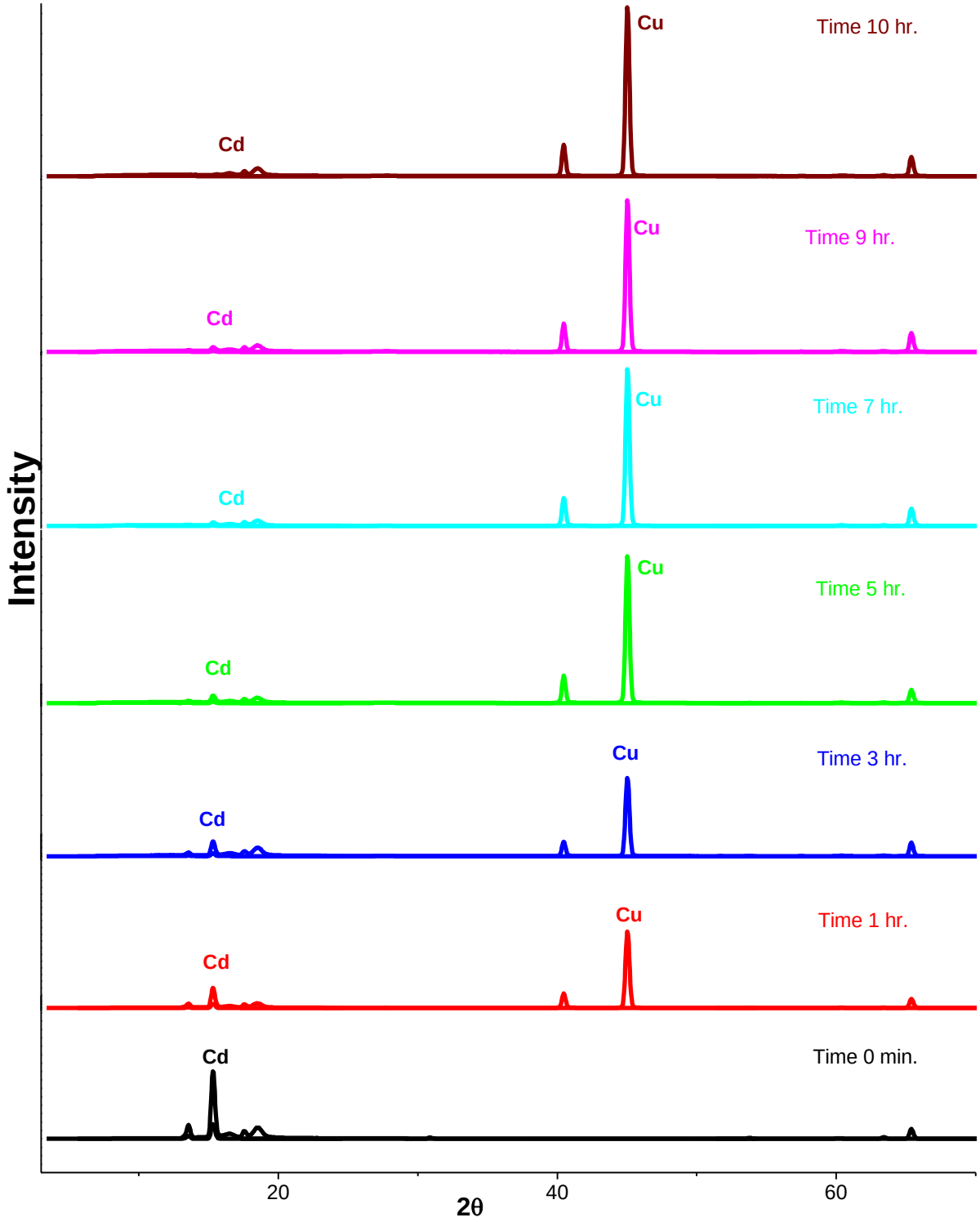
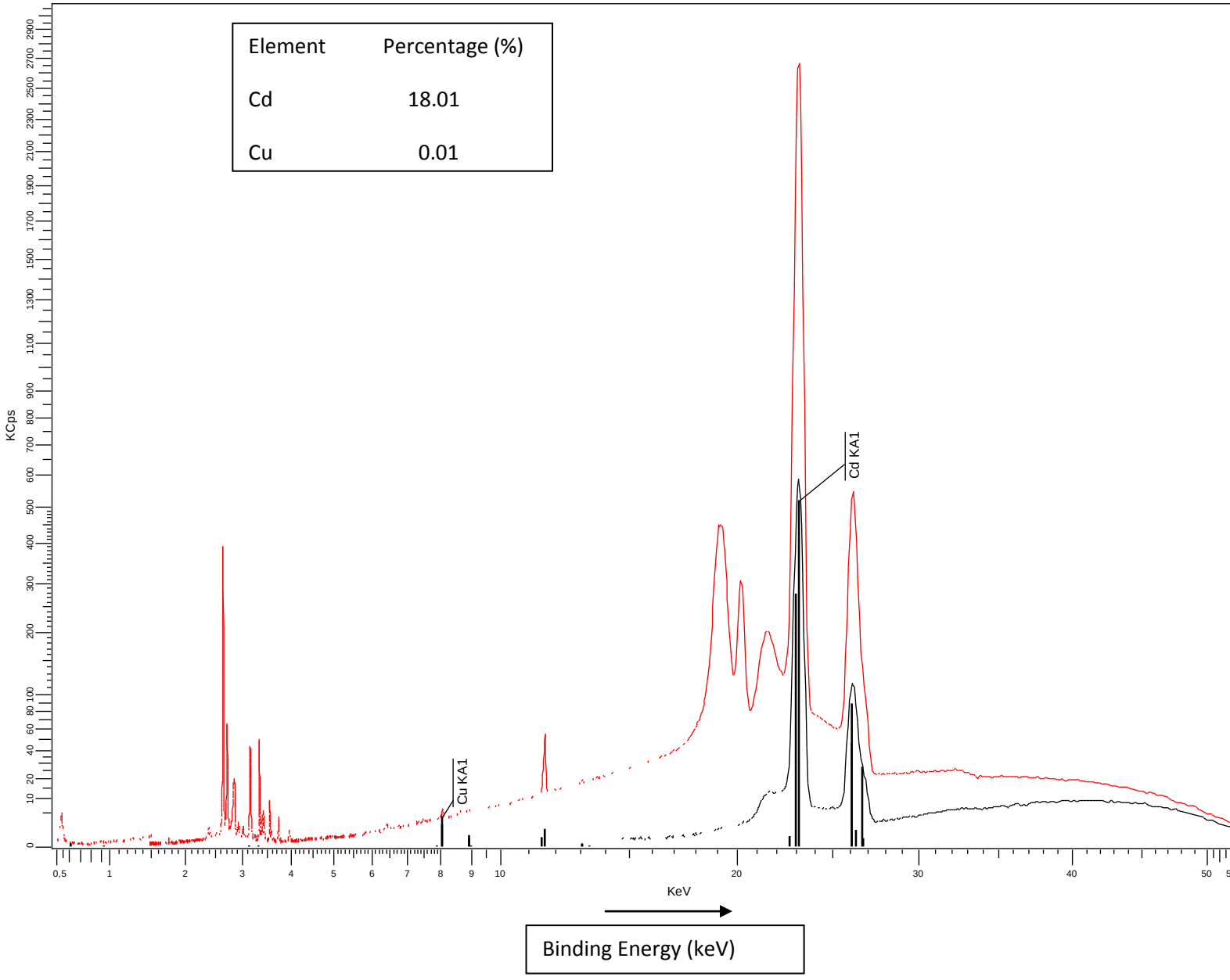
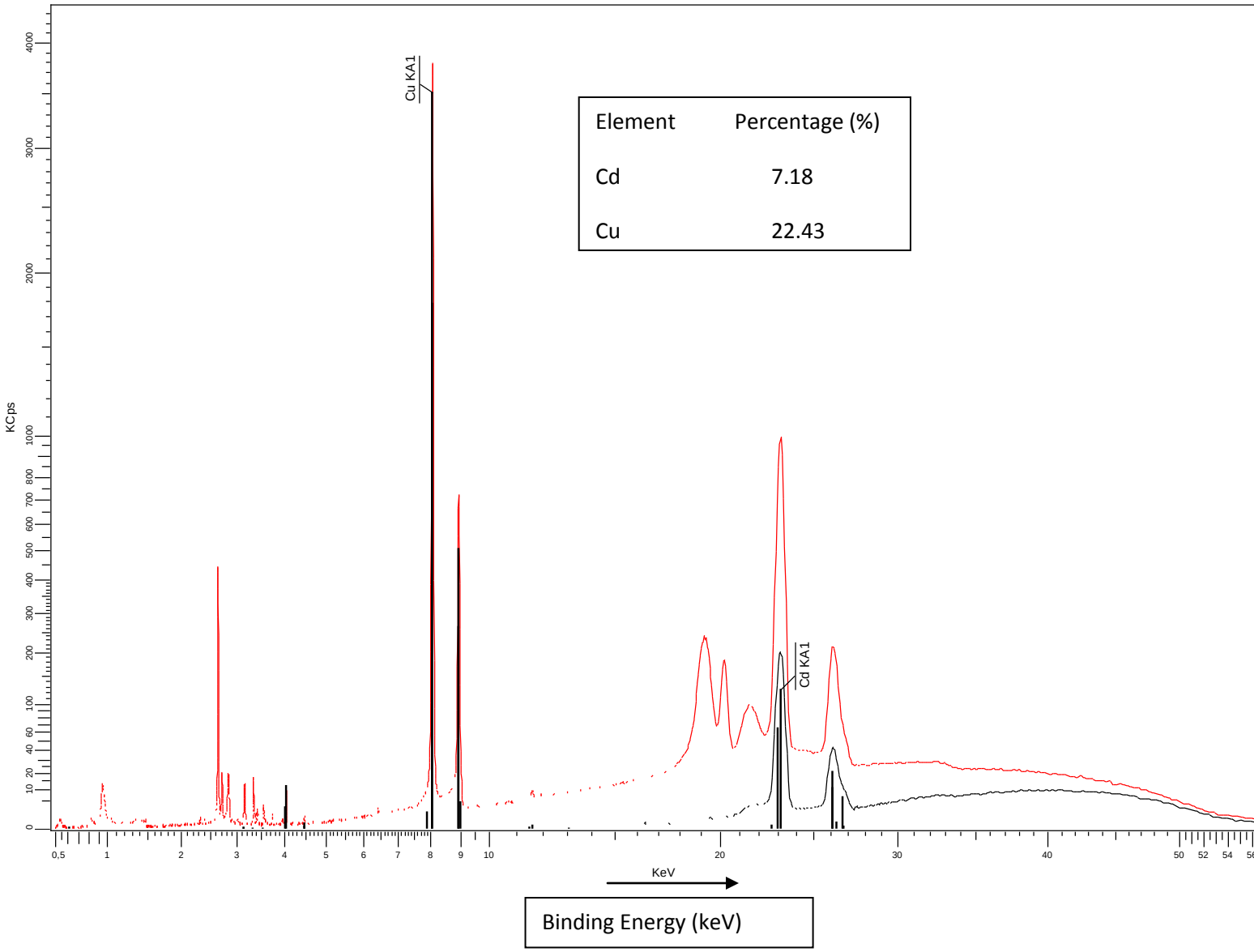


Figure S 13 WD-XRF (Intensity *vs* Binding Energy) of the Transmetallation Reaction at various intervals [CP-4-Cd + $Cu(ClO_4)_2$ → **CP-4-Cu**]

(a) At the start of the reaction (time = 0)

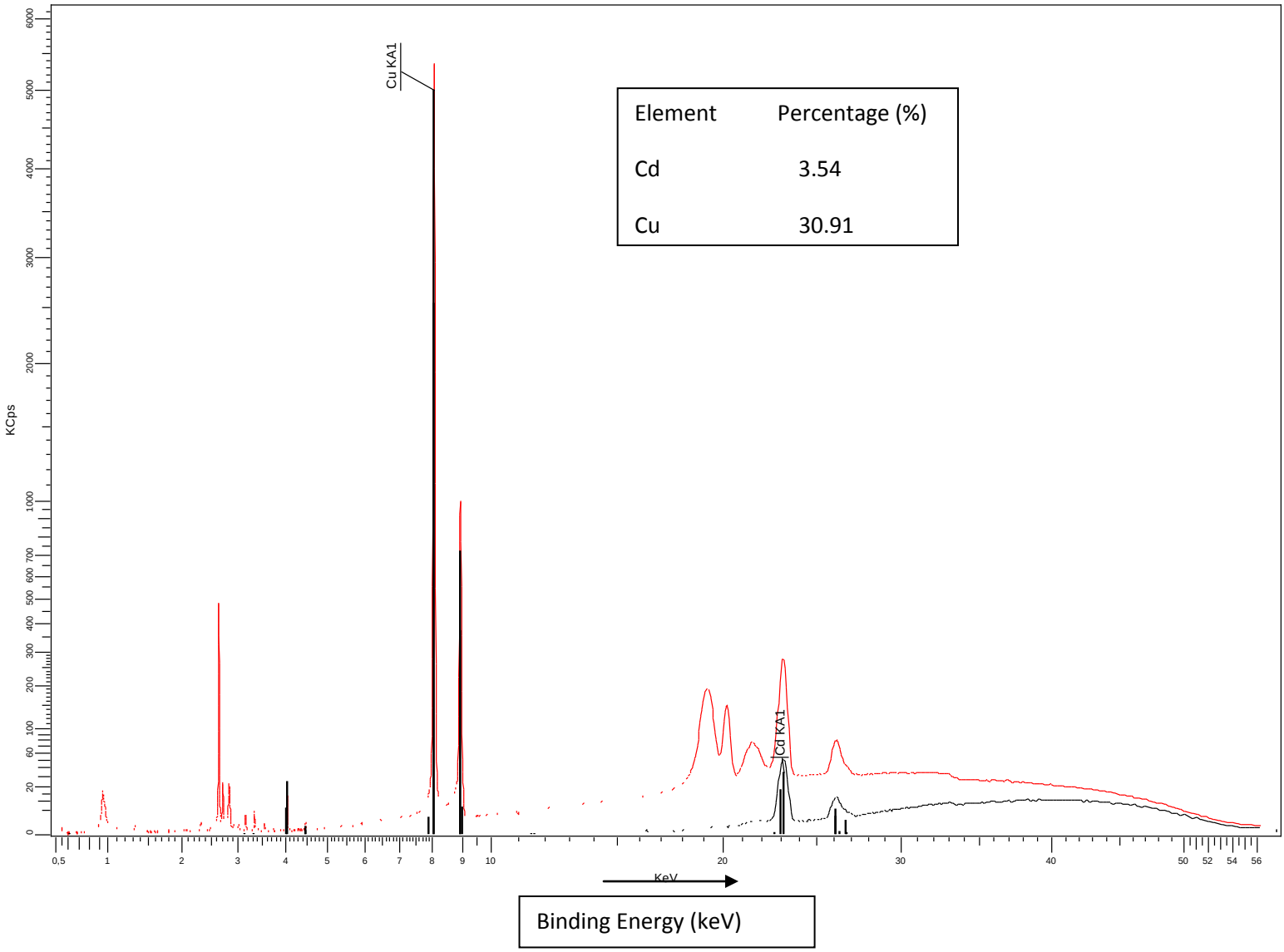


(b) After one hour of reaction

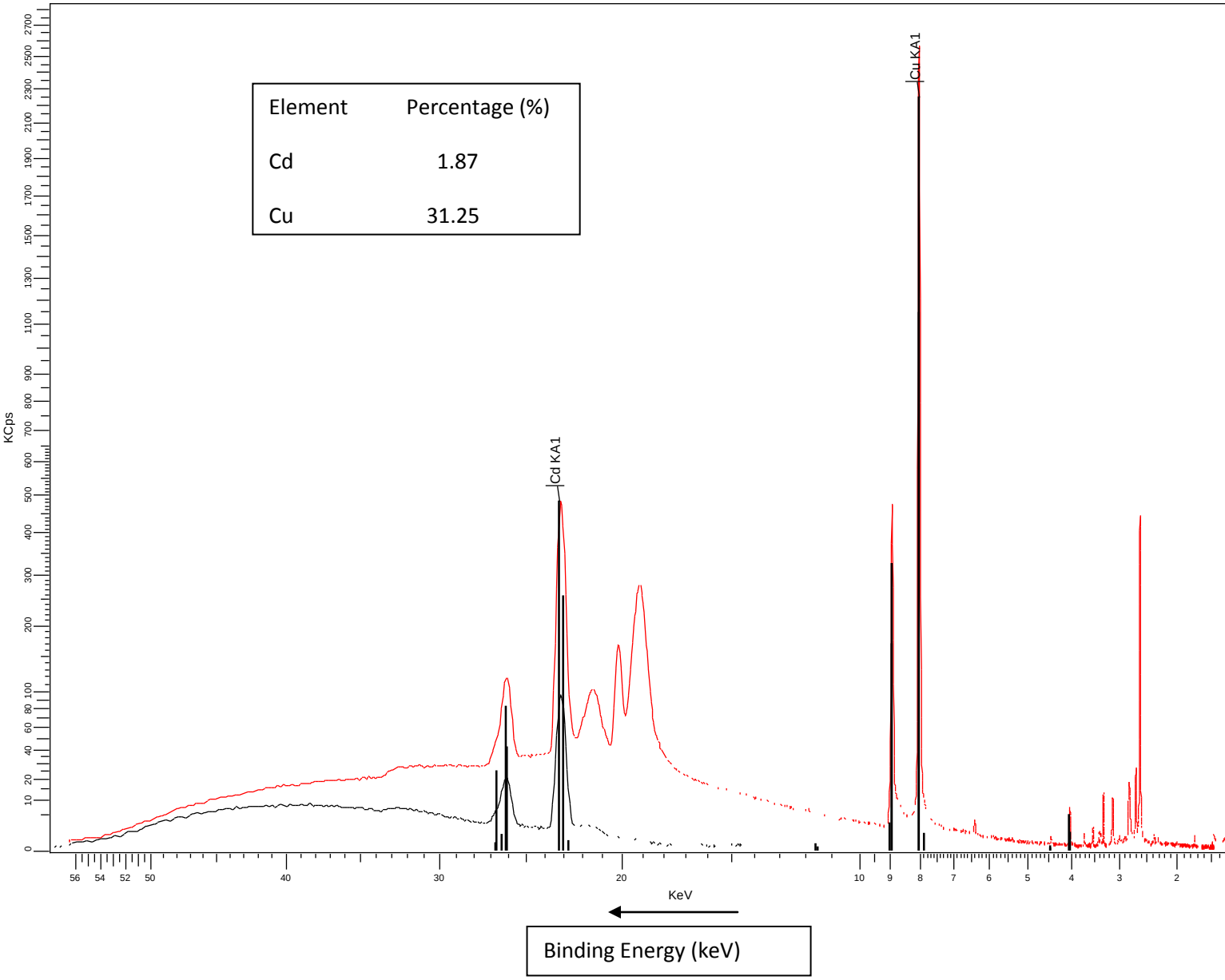


Element	Percentage (%)
Cd	7.18
Cu	22.43

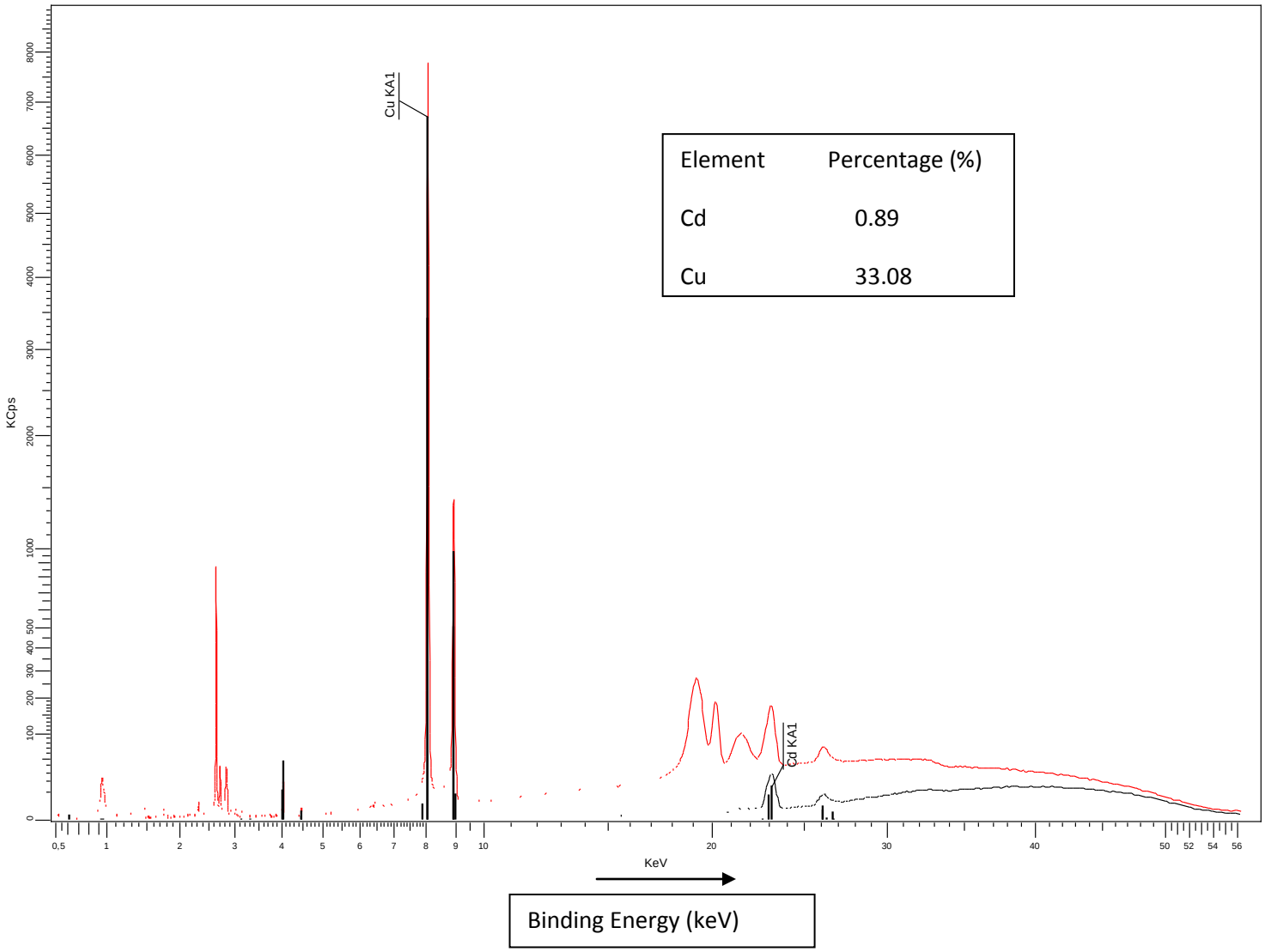
(c) After three hour of reaction



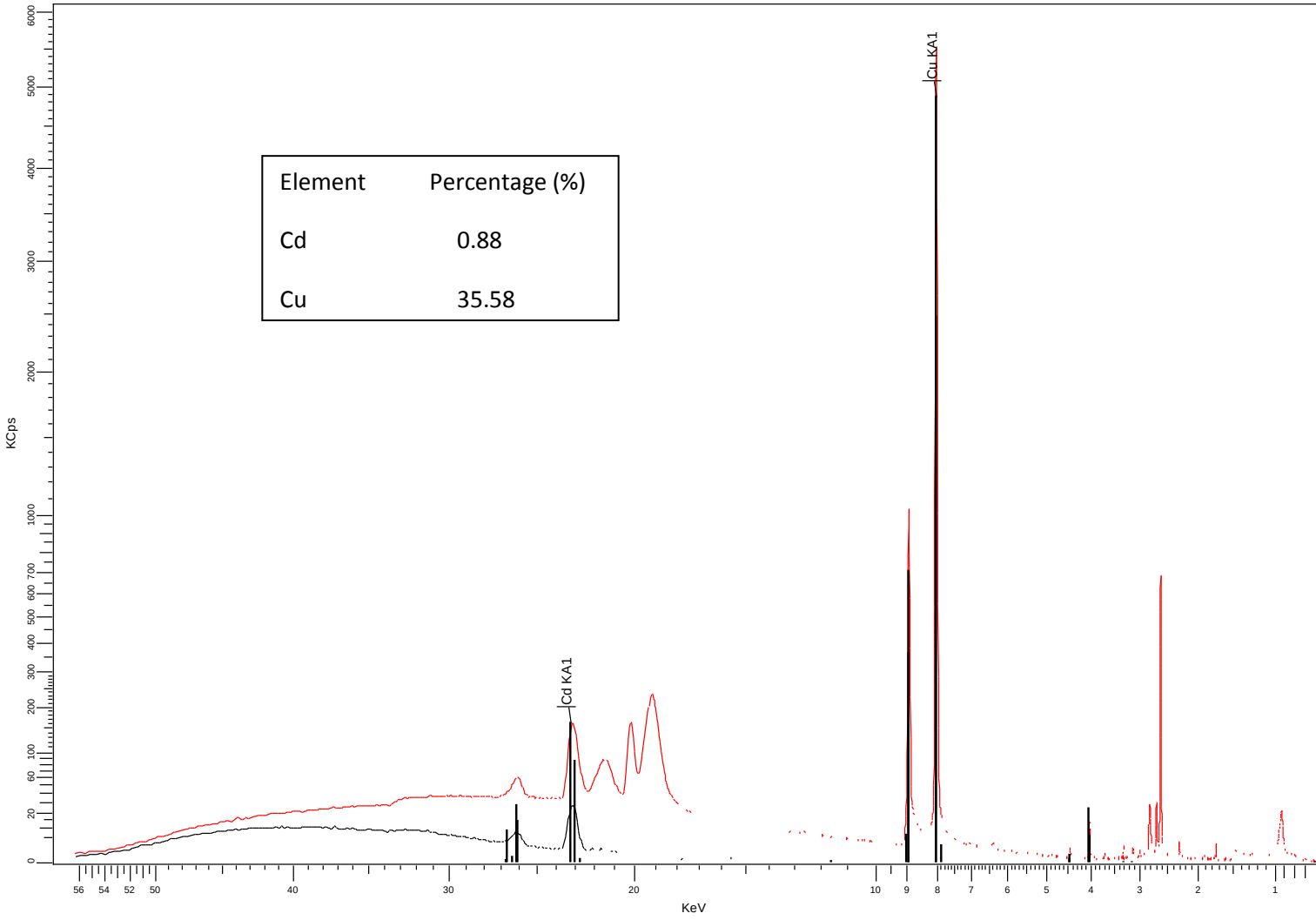
(d) After five hour of reaction



(e) After seven hour



(f) After nine hour



(g) After ten hour

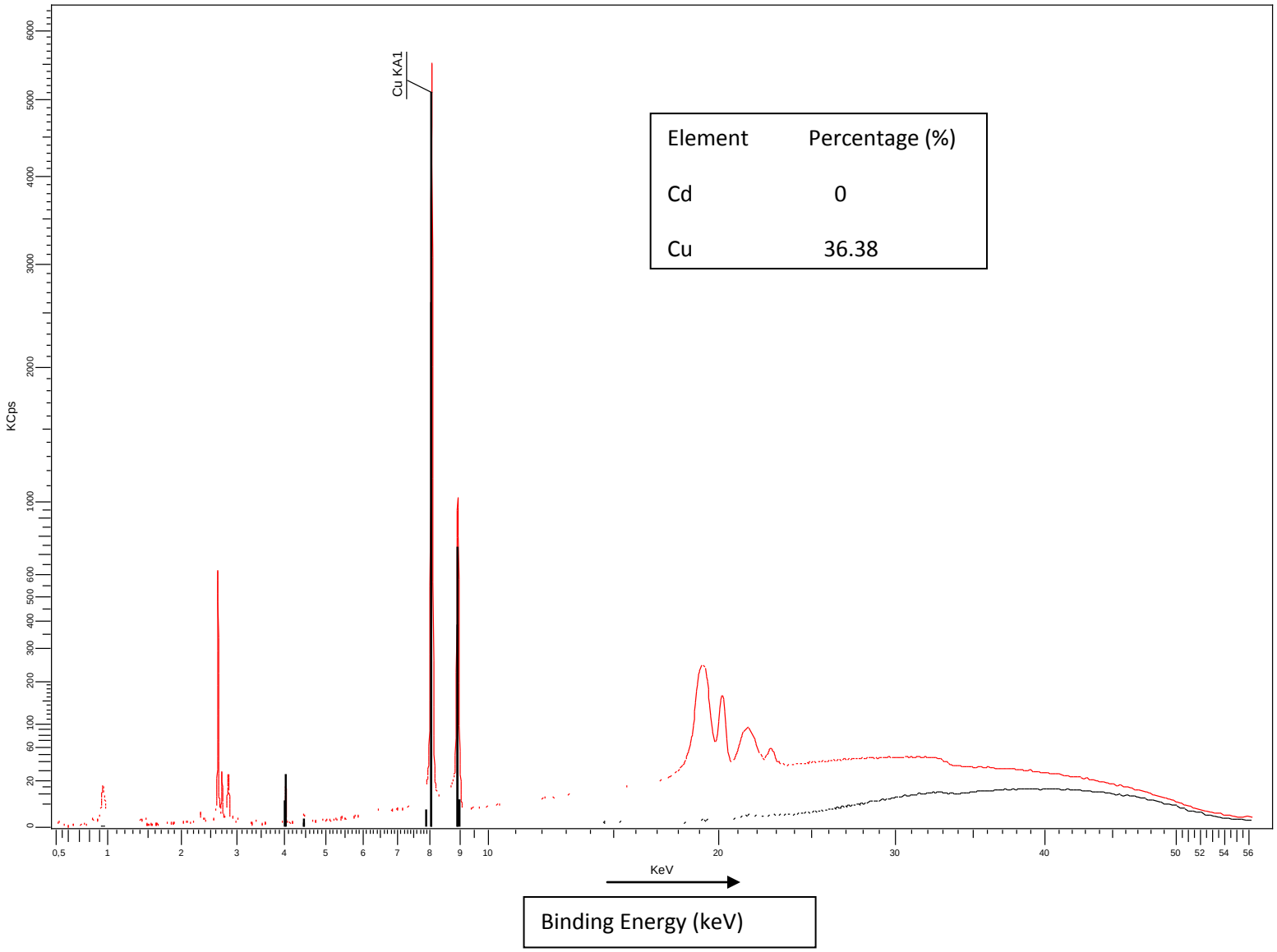


Figure S 14: ORTEP of CP-3-Cu

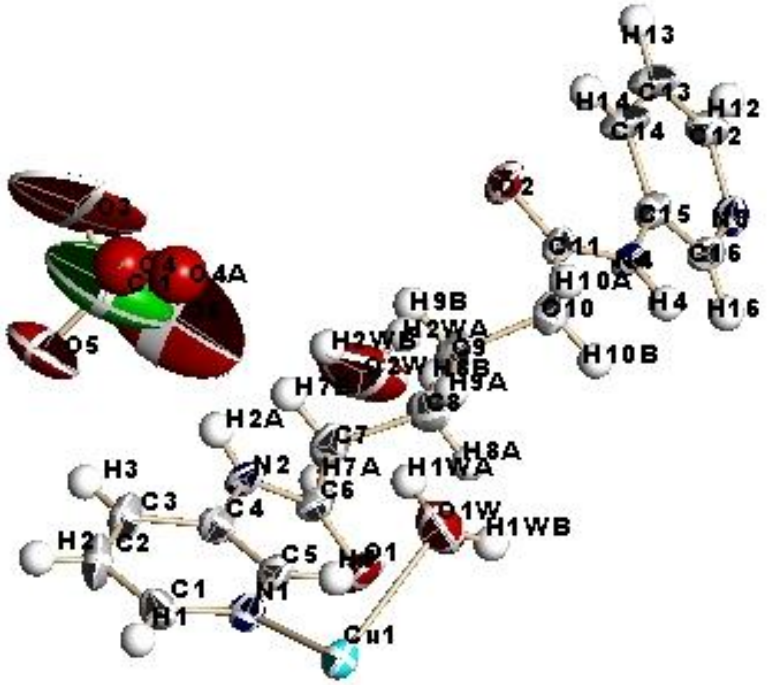
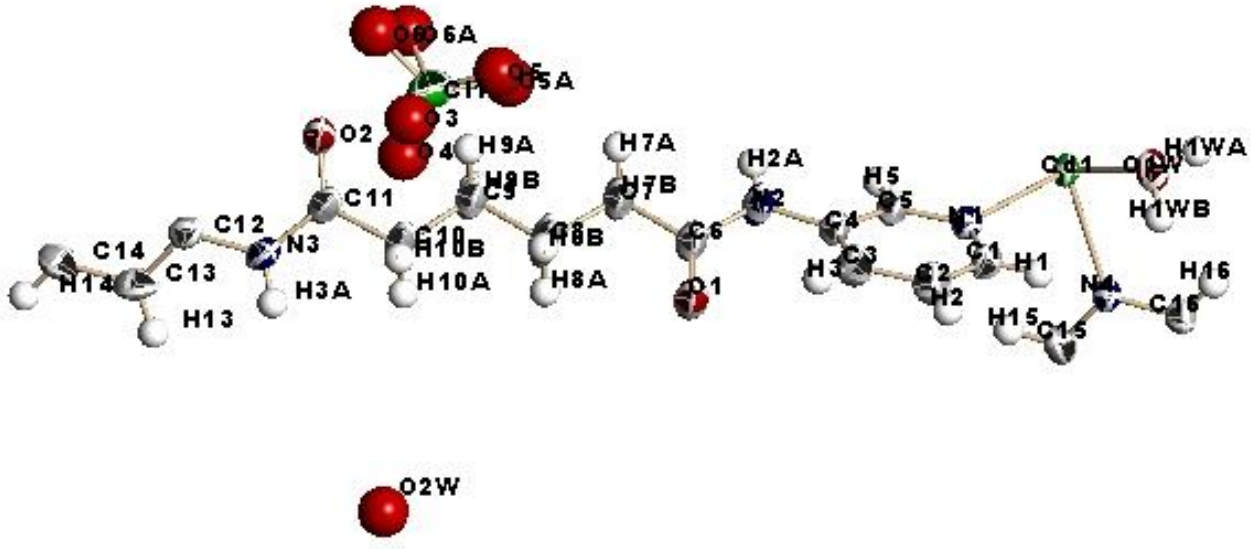


Figure S 15: ORTEP of CP-4-Cd



References:

1. *CrysAlis PRO* (oxford Diffraction, 2010, Oxford Dffraction Ltd.,Yarton, Oxfordshire, England

2. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.

3. (a) M. Sarkar and K. Biradha, *Cryst. Growth Des.*, 2006, **6**, 202; (b) L. Rajput, S, Singha and K. Biradha, *Cryst. Growth Des.*, 2007, **7**, 2788.