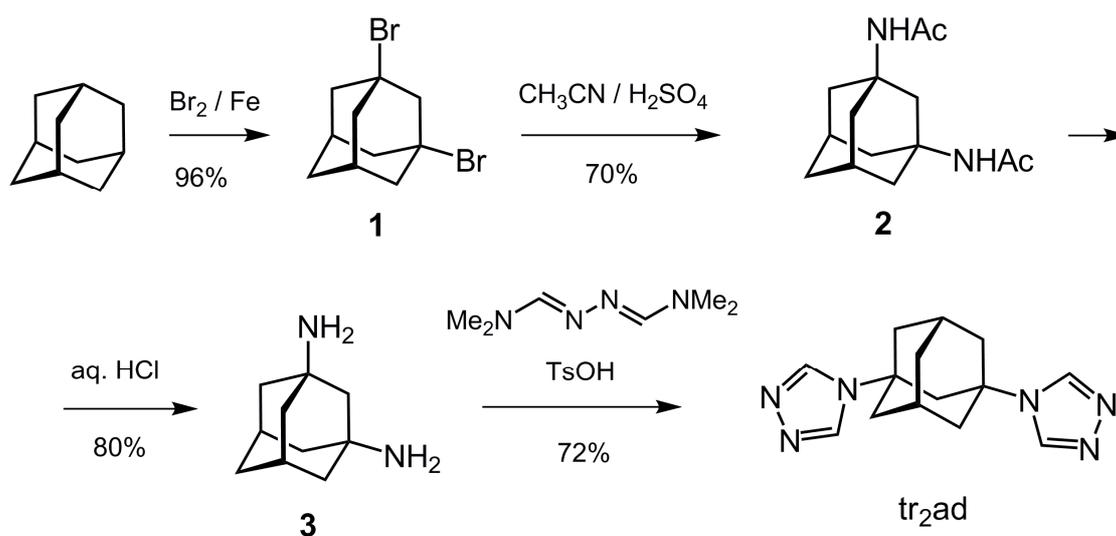


# Supplementary Materials: New Coordination Polymers of Zinc(II), Copper(II) and Cadmium(II) with 1,3-Bis(1,2,4-triazol-4-yl)adamantane

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## S1. Synthesis of the tr2ad ligand



Scheme S1. Reaction pathways for the synthesis of the tr2ad ligand.

**Synthesis of 1,3-dibromoadamantane (1, Scheme 1).** Dibromination of adamantane in a nearly quantitative yield proceeds selectively in net bromine with  $\text{FeBr}_3$  as catalyst (generated *in situ* in the presence of Fe powder), by stirring the mixture at r.t. for a short period of time (see below). In the absence of Fe, the reaction quantitatively yields the monobromide, while longer reaction periods and heating of the reaction mixture gives tribromoadamantane in high yield. Fe powder (0.88 g, 16 mmol) was added to net bromine (36.4 mL) and the mixture was stirred at r.t. for 30 min. Then, solid adamantane (12.00 g, 88 mmol) was added in one portion and stirring was continued for 1 h at r.t. until evolution of hydrogen bromide ceased. The mixture was transferred onto crushed ice (0.5 kg) mixed with solid  $\text{Na}_2\text{SO}_3$  (89 g). The precipitate was carefully reduced into powder and stirred in water containing ice until discoloration (removal of the excess bromine by reaction with sulfite). Then, the nearly colorless product (24.9 g, 96% yield) was filtered, washed with 5% aqueous HCl (50 mL) and water (50 mL), and air-dried. Colorless crystals were obtained after single crystallization from hot methanol. M.p. = 110–111 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ),  $\delta$  (ppm): 1.74 (s, 2H); 2.25 (s, 2H); 2.28 (s, 8H); 2.83 (2H).

**Synthesis of  $N,N'$ -diacetyl-1,3-diaminoadamantane (2, Scheme S1).** To a solution of 1,3-dibromoadamantane (15.60 g, 53 mmol) in acetonitrile (180 mL), concentrated  $\text{H}_2\text{SO}_4$  (91%,  $d = 1.820 \text{ g cm}^{-3}$ ) (30 mL) was added dropwise, along 30 minutes, while stirring. After a short induction period, the solution self-heated up to its boiling point. After the end of the exothermic reaction, the mixture was refluxed and stirred for 20 h. The resulting yellow-brown mixture, containing a precipitate, was transferred into cold water (400 mL) and small amounts of unidentified solid material were filtered off. The filtrate was brought to pH = 8–9 with concentrated ammonia. Then, the reaction product was extracted with chloroform ( $6 \times 100 \text{ mL}$ ). The combined extracts were dried

with  $\text{Na}_2\text{SO}_4$  and the solvent was removed with a rotary evaporator. The residual yellow oil solidified on cooling. This mass was triturated with cold acetonitrile (30 mL) to remove colored oily by-products. The insoluble colorless precipitate was filtered off, washed with cold acetonitrile (10 mL) and air-dried. The yield was 9.46 g (70 %). M.p. = 232-234 °C.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ),  $\delta$  (ppm): 1.53 (s, 2H); 1.72 (s, 6H); 1.83 (s, 8H); 2.10 (s, 4H); 7.19 (2, 2H).

**Synthesis of 1,3-diaminoadamantane (3, Scheme S1).** *N,N'*-diacetyl-1,3-diaminoadamantane (8.87 g, 35.5 mmol) was dissolved in a mixture of concentrated  $\text{HCl}_{(\text{aq})}$  (80 mL) and water (60 mL) and the solution was refluxed and stirred for 24 h. Then, the mixture was cooled to -15 °C and the colorless deposit of the 1,3-dihydrochloride (large prismatic crystals) was filtered and, without washing, air-dried at 70-80 °C (6.80 g, 80% yield). This material (4.00 g, 16.7 mmol) was dissolved in water (32 mL) and solid NaOH (1.40 g, 35 mmol) was added under stirring. The resulting alkaline solution was extracted with dichloromethane ( $6 \times 70$  mL), the organic layer was separated and evaporated to dryness. The solid residue (2.71 g) was sublimed at 140 °C and 0.1 Torr, yielding 2.56 g (92%) of pure 1,3-diaminoadamantane.

**Synthesis of 1,3-bis(1,2,4-triazol-4-yl)adamantane (tr2ad, Scheme S1).** A mixture of 1,3-diaminoadamantane (2.50 g, 150 mmol), dimethylformamide azine (10.70 g, 750 mmol),  $\text{TsOH} \cdot \text{H}_2\text{O}$  (0.43 g, 2.3 mmol) and dimethylacetamide (70 mL) was stirred at 140-150 °C for 25 h until evolution of dimethylamine ceased. The resulting brown solution was evaporated at 0.1 Torr to dryness and the brownish solid residue was triturated with acetonitrile (50 mL) and powdered under the solvent. Then, the colorless precipitate was filtered, washed with acetonitrile (20 mL) and dried at 70-80 °C (2.90 g, 72% yield), yielding single crystals of anhydrous tr2ad suitable for X-ray diffraction. Adequate single crystals of anhydrous tr2ad can also be obtained upon room-temperature crystallization from ethanol. The compound is sparingly soluble in water and slow evaporation of aqueous solutions led to the crystallization of trihydrate  $\text{tr2ad} \cdot 3\text{H}_2\text{O}$ . M.p. = 270-272 °C.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ),  $\delta$  (ppm): 1.77 (s, 2H); 2.16 (s, 8H); 2.58 (s, 2H); 3.09 (s, 2H); 8.61 (s, 4H).

## S2. Infrared spectroscopy

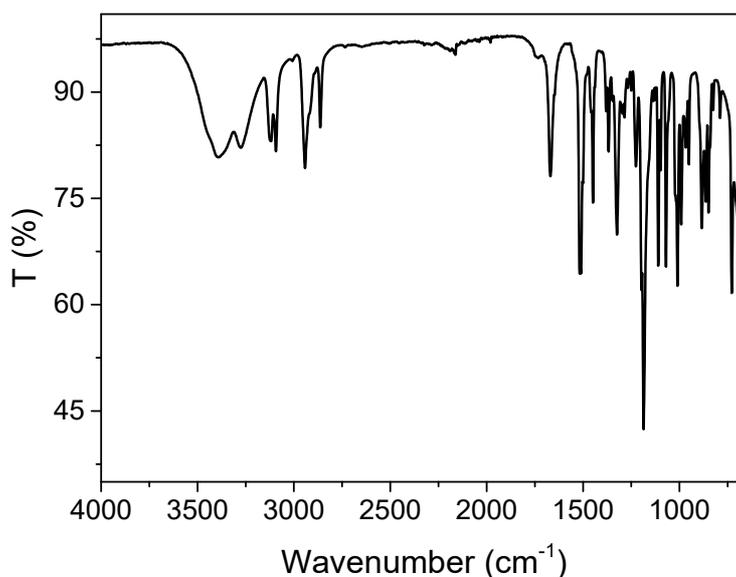
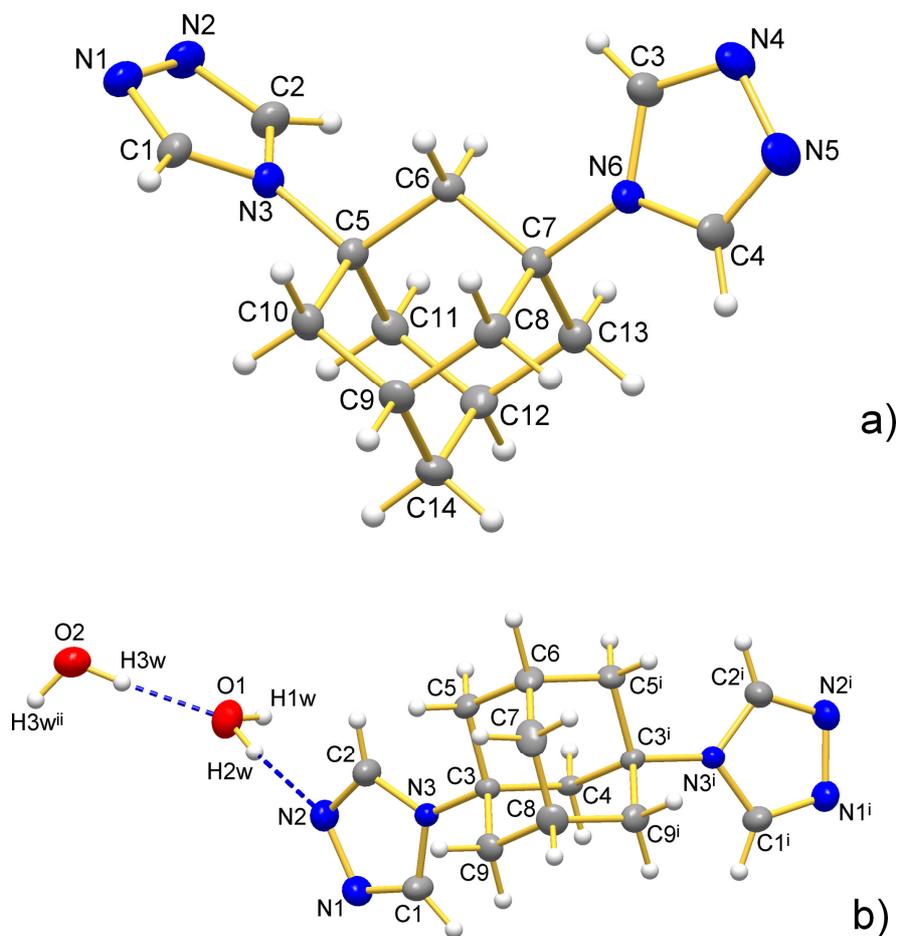
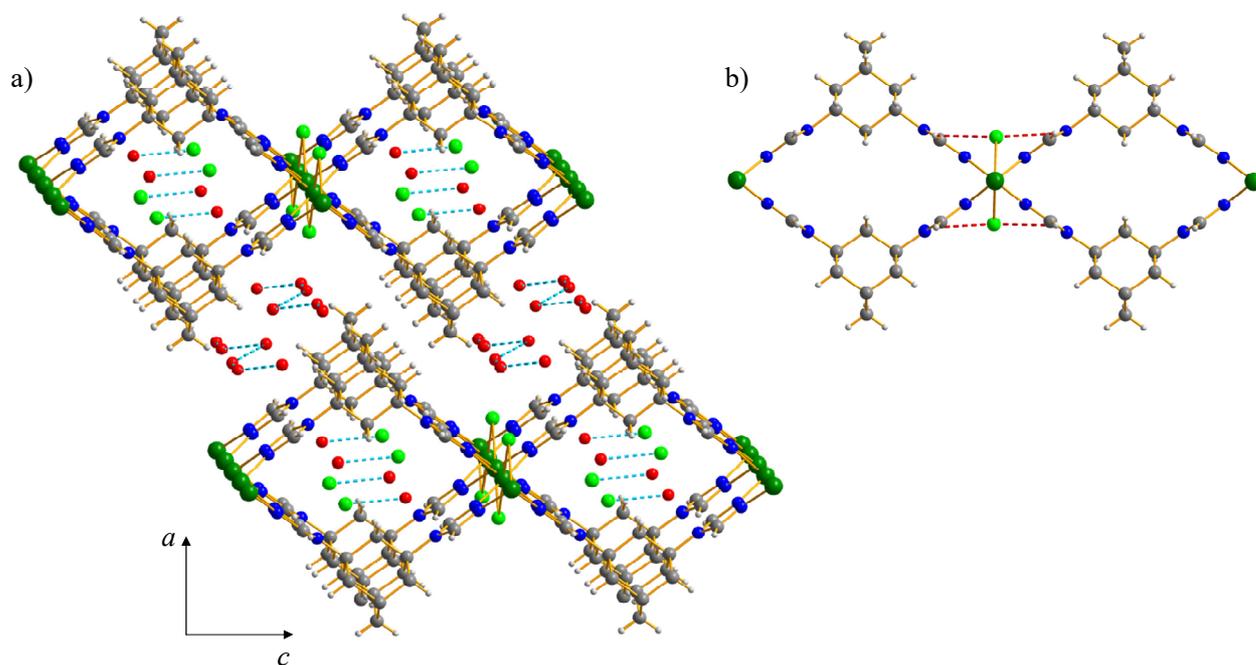


Figure 1. FTIR spectrum of 1,3-bis(1,2,4-triazol-4-yl)adamantane (tr2ad).

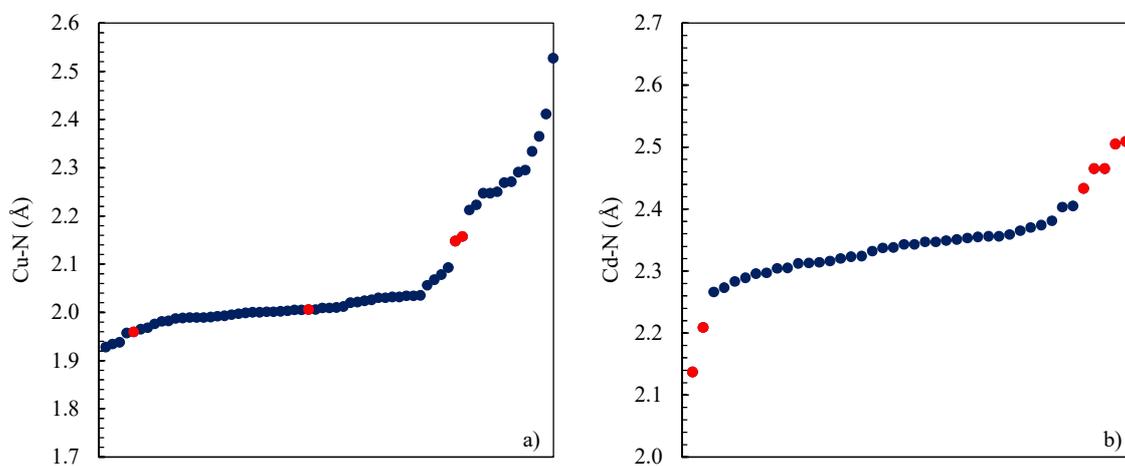
S3. Tr2ad and tr2ad·3H<sub>2</sub>O molecular structure

**Figure 2.** Ortep drawings for (a) tr2ad at 40% probability level and (b) tr2ad·3H<sub>2</sub>O 30% probability level, showing the atom labeling schemes. Atoms colour code: C, grey; H, light grey; N, blue; O, red. For tr2ad·3H<sub>2</sub>O, the C6, C7, C8 and C4 atoms of the tr2ad molecule and the O2 atom of one water molecule reside on a *m* plane. Symmetry codes: (i)  $x, 0.5-y, z$ ; (ii)  $x, 1.5-y, z$ .

#### S4. Coordination polymers crystal structure

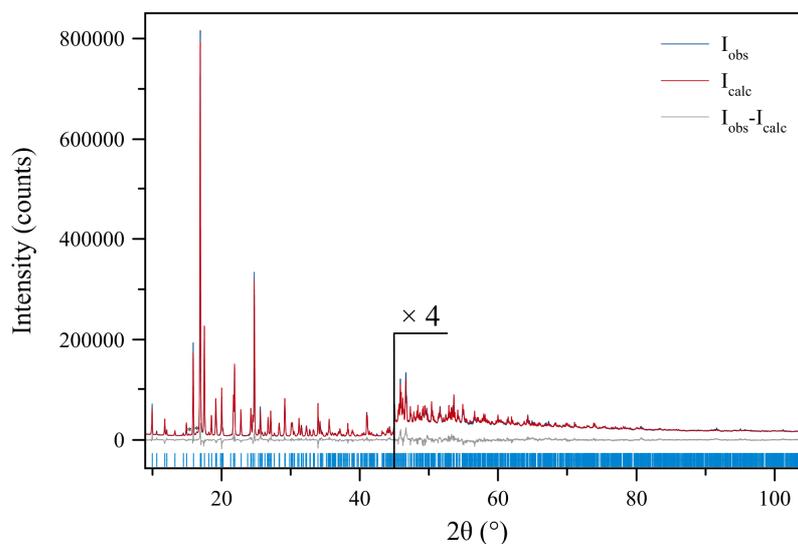


**Figure 3.** Portion of the packing of  $[[\text{Cu}(\text{tr}2\text{ad})\text{Cl}]\text{Cl}\cdot 4\text{H}_2\text{O}]_n$ , viewed (in perspective) along the  $[010]$  direction: a) the hydrogen bond interactions quoted in the text are represented with cyan dashed lines; b) the intra-layer  $\text{C-H}\cdots\text{Cl}$  non-bonding interactions quoted in the text are drawn with fuchsia dashed lines. Horizontal axis,  $c$ ; vertical axis,  $a$ . Atoms colour code: C, grey; H, light grey; Cl, light green; Cu, green; N, blue; O, red.

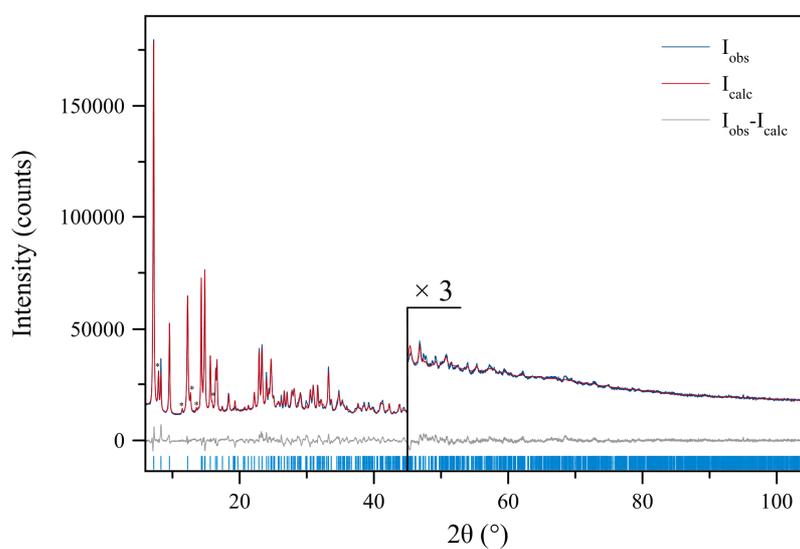


**Figure 4.** Comparison of the a) Cu-N and b) Cd-N bond distances in the title compounds (red dots) and in those known in the literature (blues dots).

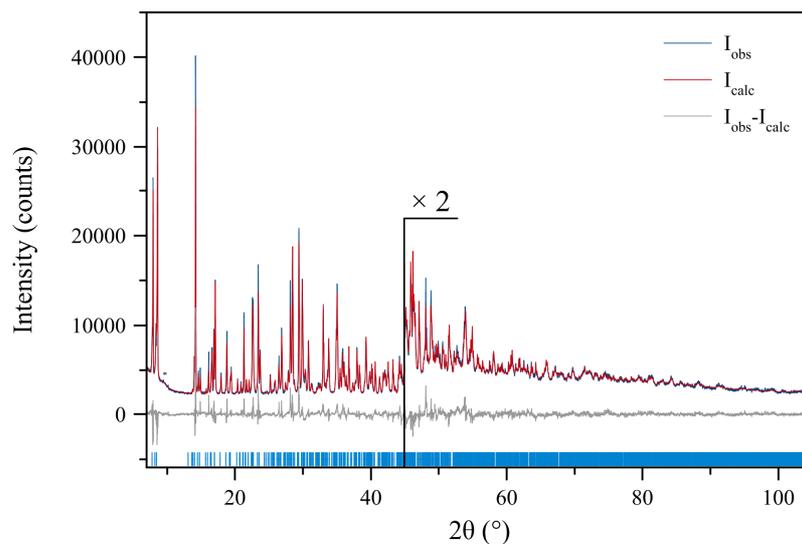
## S5. Powder X-ray diffraction structural analysis



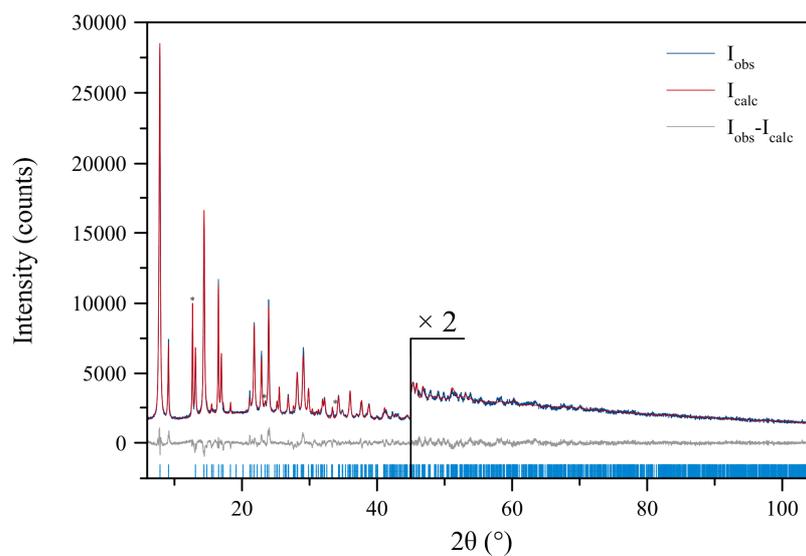
**Figure 5.** Graphical result of the final structure refinement carried out with the Rietveld method on the PXRD pattern of  $[\text{Zn}(\text{tr2ad})\text{Cl}_2]_n$  in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections. The asterisks highlight peaks belonging to impurities.  $R_{\text{Bragg}} = 0.051$ ,  $R_p = 0.057$  and  $R_{\text{wp}} = 0.078$ .



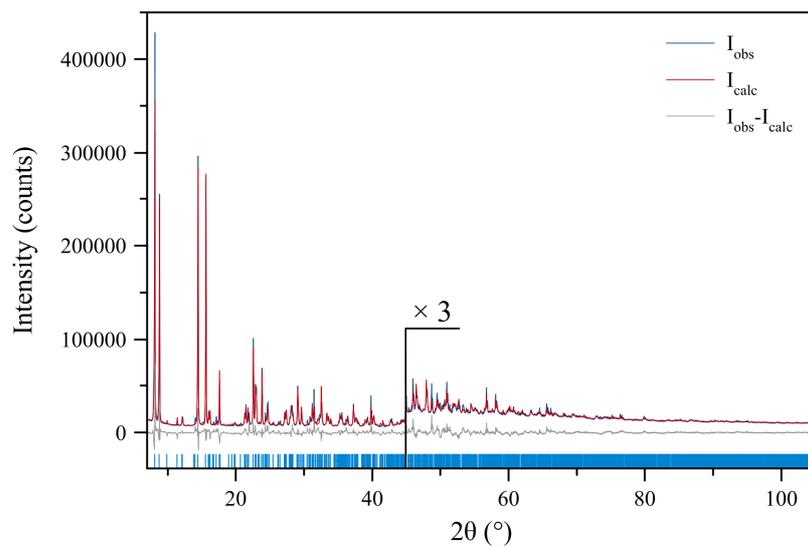
**Figure 6.** Graphical result of the final structure refinement carried out with the Rietveld method on the PXRD pattern of  $\{[\text{Cu}(\text{tr2ad})\text{Cl}]\text{Cl}\cdot 4\text{H}_2\text{O}\}_n$  in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections. The asterisks highlight peaks belonging to impurities.  $R_{\text{Bragg}} = 0.019$ ,  $R_p = 0.028$  and  $R_{\text{wp}} = 0.040$ .



**Figure 7.** Graphical result of the final structure refinement carried out with the Rietveld method on the PXRD pattern of  $[\text{Cd}_2(\text{tr}2\text{ad})\text{Cl}_4]_n$  in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections. The asterisk highlights a peak belonging to an impurity.  $R_{\text{Bragg}} = 0.050$ ,  $R_p = 0.049$  and  $R_{\text{wp}} = 0.068$ .



**Figure 8.** Graphical result of the final structure refinement carried out with the Rietveld method on the PXRD pattern of  $\{[\text{Cu}(\text{tr}2\text{ad})(\text{NO}_3)](\text{NO}_3)\}_n$  in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections. The asterisks highlight peaks belonging to impurities.



**Figure 9.** Graphical result of the final structure refinement carried out with the Rietveld method on the PXR D pattern of  $\{[\text{Cd}(\text{tr}2\text{ad})(\text{NO}_3)](\text{NO}_3)\cdot\text{H}_2\text{O}\}_n$  in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections.  $R_{\text{Bragg}} = 0.047$ ,  $R_p = 0.079$  and  $R_{\text{wp}} = 0.110$ .