

# Structural Diversity of Hydrogen-Bonded Networks of $[\text{Co}(\text{NH}_3)_6]^{3+}$ Complex Cations and Acetylenedicarboxylic Acid Anions

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The crystal structure of  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC}) \cdot 2 \text{H}_2\text{O}$  (**1**) ( $\text{ADC}^{2-}$  = acetylenedicarboxylate) ( $P2_1/n$ ,  $Z = 4$ ) was mistakenly described as containing the  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  ion [I. Stein, U. Ruschewitz, *Z. Naturforsch.* **2011**, *66b*, 471–478]. A revision is reported. While attempting to reproduce **1**, we isolated phase-pure crystalline material of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{HADC}) \cdot \text{H}_2\text{O}$  (**2**), the crystal structure of which was also reported in the article above. Upon standing in the aqueous mother liquor at room temperature for several days, the needle-shaped crystals of **2** disappear, while block-shaped crystals of the formerly unknown compound  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC})$  (**3**) grow. Satellite peaks in the X-ray diffraction frames indicate that the crystal structure is incommensurately modulated. Dissolving crystals of **3** in water at elevated temperature leads to plate-shaped crystals of the new compound  $[\text{Co}(\text{NH}_3)_6]_2(\text{ADC})_3 \cdot 3 \text{H}_2\text{O}$  (**4**) upon slow cooling to room temperature. Compounds **2–4** were investigated by elemental analysis, powder X-ray diffraction and infrared spectroscopy. Structural characterization of **4** by single-crystal X-ray analysis was also achieved ( $P\bar{1}$ ,  $Z = 2$ ). Complex **1**, however, could not be reproduced.

**Key words:** Acetylenedicarboxylic Acid, Cobalt, Coordination Compound, Crystal Structure, Hydrogen Bonding

## Introduction

Polytopic carboxylato ligands with suitable spacer groups between the carboxylate moieties are a frequent choice for coordination polymers [1–4]. The dianion of acetylenedicarboxylic acid ( $\text{H}_2\text{ADC}$ ) belongs to this class of bridging ligands. In  $\text{H}_2\text{ADC}$ , the two carboxyl groups are separated by a rigid ethynyl spacer group (Scheme 1(a)). The first coordination networks of  $\text{ADC}^{2-}$  were reported by Robl and Hentschel in the early 1990s [5, 6]. In the meantime we [7–21], and others [22–42] have studied a wide variety of  $\text{ADC}^{2-}$ -based coordination polymers.  $\text{ADC}^{2-}$ -linked dumbbell-shaped [34, 43–46] and macrocyclic discrete supramolecular metal complexes [47] have also been described. In contrast, structurally characterized coordination compounds of  $\text{HADC}^-$  are scarce [48–50].

$\text{HADC}^-$  and  $\text{ADC}^{2-}$  feature multiple hydrogen bonding donor and/or acceptor sites, and a number of hydrogen-bonded structures can be found in the literature [41, 51–66]. We have also investigated some hydrogen-bonded networks containing  $\text{HDAC}^-$  and/or  $\text{ADC}^{2-}$  building blocks [67–69]. In this context, we reported a structural study of hydrogen-bonded  $\text{HDAC}^-$  salts with hexamine or hexaaqua complex cations in which we incorrectly postulated the formation of the compound  $[\text{Co}(\text{H}_2\text{O})_6](\text{ADC})(\text{HADC}) \cdot 2 \text{H}_2\text{O}$  (“**1**”) (CSD refcode: ASAWOH) [69], containing the unstable  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  cation.

The initial aim of the present study was to revisit the crystal structure of “**1**”. However, while unsuccessfully attempting to resynthesize crystals of “**1**”, we obtained phase-pure bulk material of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{HADC}) \cdot \text{H}_2\text{O}$  (**2**). The crystal struc-

ture of **2** was reported previously (CSD refcode: ASAWUN) [69], but the bulk sample did not contain a single phase at that time. We have now discovered that when a sample of **2** is left under ambient conditions in the mother liquor containing  $\text{H}_2\text{ADC}$ , the needle-shaped crystals of **2** slowly vanish over a period of several weeks and are replaced by block-shaped crystals of  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC})$  (**3**). Dissolving **3** in hot water and subsequent cooling leads to  $[\text{Co}(\text{NH}_3)_2(\text{ADC})_3 \cdot 3\text{H}_2\text{O}$  (**4**), whose crystal structure was elucidated by single-crystal X-ray analysis. In the present contribution, we report a re-refinement of the single-crystal X-ray data of “**1**” and revise its composition to  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC}) \cdot 2\text{H}_2\text{O}$  (**1**), containing the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex cation. Moreover, we describe the synthesis of **2–4**, which were characterized by elemental analysis, powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy, and discuss the structural diversity of hydrogen-bonded networks with  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex cations and acetylenedicarboxylic acid mono- and/or dianions.

## Results and Discussion

### Revision of the crystal structure of **1**

In our publication of 2011 [69], we misinterpreted the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  complex ion in the crystal structure of  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC}) \cdot 2\text{H}_2\text{O}$  (**1**) as  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ , *i. e.* nitrogen was incorrectly assigned as oxygen. Incorrect atom type assignment is not an uncommon error in crystal structure analysis [70], particularly when neighboring atoms in the Periodic Table are involved. The error in the original study [69] was exacerbated by the absence of an elemental analysis for **1**, which could not be conducted because no phase-pure material was available, and the inability to correctly identify all hydrogen atoms in the difference electron density map, with the result that the ammine ligands were mistaken for aqua ligands. Our original work was mainly focused on the  $\text{ADC}^{2-}$  and  $\text{HADC}^-$  anions and the hydrogen-bonded networks that are formed with these linkers. Compound **1** was originally synthesized from  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  under ambient conditions. Chemical experience suggests that the ammine ligands should not be replaced by aqua ligands during the reaction, since Co(III) complexes with low-spin  $d^6$  electronic configuration are known to be relatively in-

ert towards ligand substitution. Moreover, according to Brønsted, the  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  ion cannot exist, owing to the tendency of heteroleptic ammine aqua Co(III) complexes to take up an electron, forming hydroxido complexes with an increasing number of aqua ligands [71]. From these considerations it is now clear that we misinterpreted the single-crystal X-ray data in the original work [69].

To clarify the chemical composition of **1**, we started intensive efforts to repeat the synthesis of **1**, but none of these attempts has been successful so far. Thus, characterization of **1** by analytical methods other than single-crystal X-ray diffraction is not possible at the moment. However, the orange color reported for the crystal studied in [69], which is similar to the color of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , supports our proposition that  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is present in **1**. Reexamination of the original single-crystal X-ray diffraction data assuming the composition  $[\text{Co}(\text{H}_2\text{O})_6](\text{ADC})(\text{HADC}) \cdot 2\text{H}_2\text{O}$  gave Hirshfeld rigid-bond tests and checkCIF alerts arising from largely differing atomic displacement parameters of bonded atoms, which are an indication of an incorrect atom type assignment in the coordination sphere of Co(III) [70, 72]. The Co–N bond lengths and the hydrogen bonding scheme are also consistent with a  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion being present in the crystal structure of **1**. Accordingly, the crystal structure of **1** was re-refined using the original data with  $[\text{Co}(\text{NH}_3)_6]^{3+}$  instead of  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  as the cation. In the final difference Fourier maps we have now been able to localize all protons of the ammine ligand. A revised description of the crystal structure of **1** is given below.

Figure 1 shows a displacement ellipsoid plot of the asymmetric unit of **1**. Selected bond lengths and angles

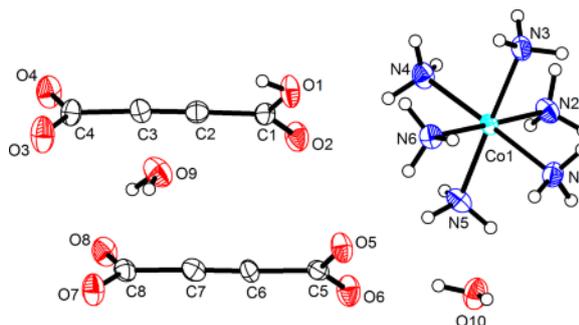


Fig. 1. Asymmetric unit of **1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by small spheres of arbitrary radii.

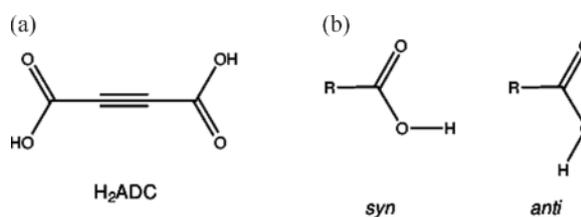
Table 1. Bond lengths (Å) and angles (deg) for the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion in **1** and **4** with estimated standard deviations in parentheses.<sup>a</sup>

<b>1</b>					
Co1–N1	1.967(4)	Co1–N3	1.965(4)	Co1–N5	1.966(4)
Co1–N2	1.971(3)	Co1–N4	1.968(4)	Co1–N6	1.964(3)
N1–Co1–N2	90.66(16)	N2–Co1–N4	91.07(16)	N4–Co1–N6	88.51(15)
N1–Co1–N3	90.30(16)	N2–Co1–N5	88.95(15)	N5–Co1–N6	91.98(16)
N1–Co1–N5	89.31(16)	N3–Co1–N4	90.44(17)	N1–Co1–N4	178.13(16)
N1–Co1–N6	89.78(15)	N3–Co1–N6	89.73(16)	N2–Co1–N6	178.97(17)
N2–Co1–N3	89.34(15)	N4–Co1–N5	90.00(16)	N3–Co1–N5	178.24(16)
<b>4</b>					
Co1–N1	1.9640(8)	Co1–N3	1.9721(7)	Co1–N5	1.9639(7)
Co1–N2	1.9640(7)	Co1–N4	1.9673(7)	Co1–N6	1.9607(8)
N1–Co1–N2	90.62(3)	N2–Co1–N5	90.58(3)	N4–Co1–N6	90.53(3)
N1–Co1–N3	88.73(4)	N2–Co1–N6	89.22(3)	N5–Co1–N6	88.87(3)
N1–Co1–N4	89.63(3)	N3–Co1–N4	90.35(3)	N1–Co1–N6	179.77(3)
N1–Co1–N5	90.97(3)	N3–Co1–N6	91.43(4)	N2–Co1–N4	179.66(3)
N2–Co1–N3	89.88(3)	N4–Co1–N5	89.19(3)	N3–Co1–N5	179.46(3)
Co2–N7	1.9667(8)	Co2–N8	1.9631(7)	Co2–N9	1.9619(7)
Co2–N7a	1.9668(8)	Co2–N8a	1.9631(7)	Co2–N9a	1.9619(7)
N7–Co2–N8	89.78(3)	N8–Co2–N7a	90.22(3)	N7a–Co2–N9a	88.68(3)
N7–Co2–N9	88.68(3)	N8–Co2–N9a	91.74(3)	N8a–Co2–N9a	88.26(3)
N7–Co2–N8a	90.22(3)	N9–Co2–N7a	91.32(3)	N7–Co2–N7a	180
N7–Co2–N9a	91.32(3)	N9–Co2–N8a	91.74(3)	N8–Co2–N8a	180
N8–Co2–N9	88.26(3)	N7a–Co2–N8a	89.78(3)	N9–Co2–N9a	180
Co3–N10	1.9581(8)	Co3–N11	1.9566(8)	Co3–N12	1.9702(8)
Co3–N10b	1.9581(8)	Co3–N11b	1.9566(8)	Co3–N12b	1.9702(8)
N10–Co3–N11	90.49(4)	N11–Co3–N10b	89.51(4)	N10b–Co3–N11b	90.49(4)
N10–Co3–N12	89.91(4)	N11–Co3–N12b	92.02(4)	N10b–Co3–N12b	89.90(4)
N10–Co3–N11b	89.51(4)	N12–Co3–N10b	90.10(4)	N10–Co3–N10b	180
N10–Co3–N12b	90.09(4)	N12–Co3–N11b	92.03(4)	N11–Co3–N11b	180
N11–Co3–N12	87.97(4)	N11b–Co3–N12b	87.98(4)	N12–Co3–N12b	180

<sup>a</sup> Symmetry codes: (a)  $1-x, 1-y, -z$ ; (b)  $2-x, -y, -z$ .

for the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion are given in Table 1. The N–Co–N bond angles show that the six ammine ligands surround Co1 with little distortion from the regular octahedral geometry. The Co–N bond lengths are as expected [73], with a mean value of 1.967(2) Å. This compares well with the average Co–N bond length for 57 crystal structures containing the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion (with 516 Co–N distances) reported in the Cambridge Structural Database (CSD; Version 5.34, with updates to May 2013 [74, 75]), which is 1.961(2) Å. The carboxylic group of the  $\text{HADC}^-$  ion was found in the *anti*-conformation (Scheme 1(b)), facilitating an  $\text{O} \cdots \text{H}$  hydrogen bond to a neighboring  $\text{ADC}^{2-}$  ion. The corresponding C1–O1 bond length is 1.296(5) Å, whereas the other C–O bonds are, as expected, shorter (1.23–1.27 Å). The dihedral angle between the mean planes of the COO moieties is 50.2(4) and 45.6(4)° for the  $\text{HADC}^-$  and  $\text{ADC}^{2-}$  ion, respectively. The C1–

C2, C3–C4, C5–C6 and C7–C8 bond lengths lie within the range of 1.45–1.48 Å. As is consistent with their triple bond character, the C2–C3 and C6–C7 bonds are significantly shorter at 1.203(6) and 1.192(6) Å, respectively, with the bond angles at C2, C3, C6 and C7 deviating slightly from linearity (177.0–179.1°). Figure 2 depicts the contents of the monoclinic unit



Scheme 1. (a) Formula diagram of acetylenedicarboxylic acid ( $\text{H}_2\text{ADC}$ ); (b) low-energy conformations of the carboxylic group.

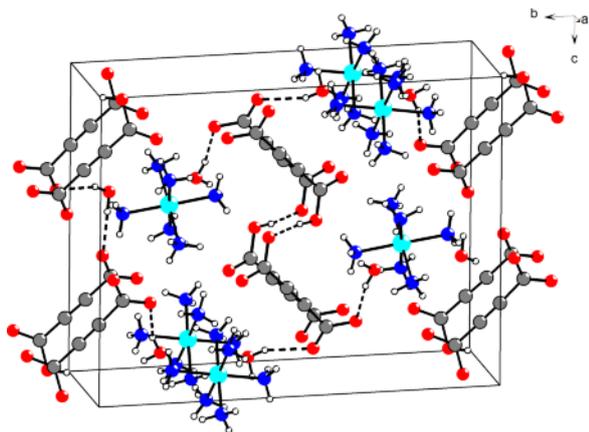


Fig. 2. (color online). The monoclinic unit cell of **1**, viewed approximately along the [100] direction. For the sake of clarity only O–H...O hydrogen bonds are illustrated by dashed lines. Color scheme: grey, carbon; blue, nitrogen; red, oxygen; turquoise, cobalt; white, hydrogen.

cell of **1**. The packing of the ions and water molecules is dominated by O–H...O and N–H...O hydrogen bonding interactions. The  $\text{HADC}^-$  and  $\text{ADC}^{2-}$  ions form discrete pairs through O–H...O<sup>-</sup> hydrogen bonds (graph set descriptor: D [76]). The O...O distance of 2.523(4) Å and the angle at the hydrogen atom of 172° are indicative of strong interanion O–H...O<sup>-</sup> hydrogen bonds [77]. The existence of this hydrogen bond is consistent with Etter's third hydrogen bond rule, which states that the best hydrogen bond donors and acceptors (excluding intramolecular hydrogen bonds) form hydrogen bonds to one another [78]. The water molecules act as hydrogen bond donors to carboxylate oxygen atoms of  $\text{HADC}^-$  and  $\text{ADC}^{2-}$  (O...O distances: 2.77–3.02 Å; O–H...O angles: 157.2–169.0°) and as acceptors for ammine hydrogen atoms of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . The  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ions furthermore form hydrogen bonds to carboxylic and carboxylate oxygen atoms of  $\text{HADC}^-$  and  $\text{ADC}^{2-}$ . The N...O distances are in the range 2.89–3.46 Å with N–H...O angles in the range 130–176°: Both are characteristic of moderate to weak N–H...O hydrogen bonds. The description of the complex cation as  $[\text{Co}(\text{NH}_3)_6]^{3+}$  rather than  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  clearly results in a more sensible, but also more complicated overall hydrogen bonding scheme, since each ammine ligand exhibits at least three short N–H...O distances to neighboring hydrogen bond acceptors. Thus, there is no conflict within the N–H...O hydrogen

bonding pattern between the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ions and the surrounding oxygen atoms as hydrogen bond acceptors, lending support to the view that **1** contains  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ions and not  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  ions.

#### Synthesis and characterization of **2–4**

Reaction of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  with  $\text{H}_2\text{ADC}$  in a 1 : 2 molar ratio in water afforded orange needle-shaped crystals of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{HADC}) \cdot \text{H}_2\text{O}$  (**2**). In contrast to the previous study [69], PXRD and elemental analysis of the crystalline bulk material have shown that **2** re-synthesized by this method essentially comprises one crystalline phase. Figure 3 compares the experimental PXRD pattern of the bulk material with that calculated from the single-crystal data (CSD refcode: ASAWUN). In view of the reassignment of the crystal structure of **1**, it is instructive to look at the crystal structure of **2** in more detail (Fig. 4). The crystal structure of **2** at room temperature exhibits  $Pnma$  space group symmetry with  $Z = 4$ . All building blocks contain a crystallographic mirror plane perpendicular to [010]. The molecular geometry parameters of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $\text{HADC}^-$  ions are as expected and similar to those in **1**, except for the dihedral angle of the mean planes of the carboxylic and carboxylate groups of  $\text{HADC}^-$ , which increases from 50.2(4)° in **1** to 90.0(1)° in **2** [69]. In contrast to **1**, however, the carboxylic group of  $\text{HADC}^-$  adopts the *syn*-

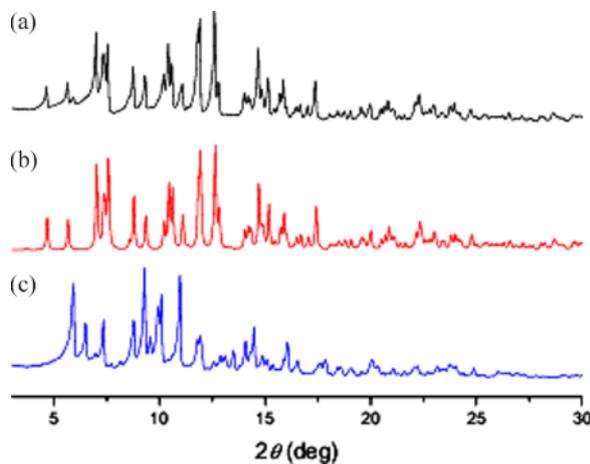


Fig. 3. Comparison of PXRD patterns of **2** and **3**: (a) experimental pattern for bulk material of **2**, (b) theoretical pattern of **2** calculated from the single-crystal structure (CSD refcode: ASAWUN), and (c) experimental pattern for bulk material of **3**.

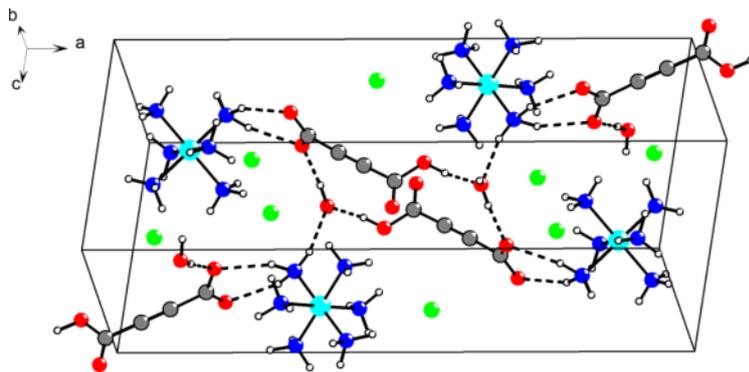


Fig. 4. (color online). View of the orthorhombic unit cell of **2** (CSD refcode: ASAWUN). O–H···O and N–H···O hydrogen bonds are represented by dashed lines. Those of the N–H···Cl type are omitted for clarity. Color scheme: grey, carbon; blue, nitrogen; red, oxygen; green, chlorine; turquoise, cobalt; white, hydrogen.

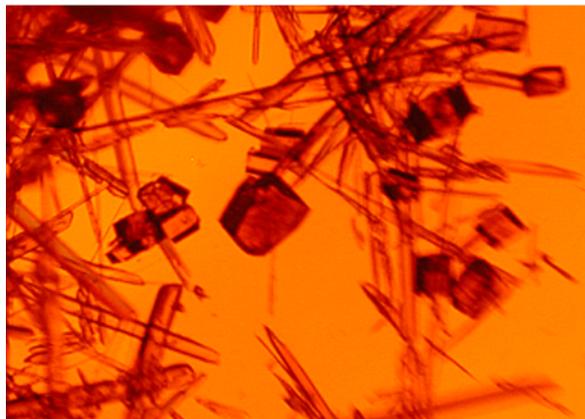
conformation (Scheme 1(b)). No interanion O–H···O hydrogen bonds are found, but the carboxylic group forms a short hydrogen bond to the water molecule in a  $C_S$ -symmetric arrangement [O···O: 2.493(4) Å; O–H···O: 171 (5)°; graph set descriptor: D]. In turn, the water molecules link the carboxylate groups of  $\text{HADC}^-$  ions into polymeric hydrogen-bonded chains [O···O: 2.676(3) Å; O–H···O: 173 (5)°; graph set descriptor:  $C_2^2(6)$ ] along the [010] direction. The N···O hydrogen bonding distances are significantly longer. An ammine ligand forms a hydrogen bond to the remaining acceptor site of the water molecule [N···O: 3.052(5) Å; N–H···O: 164°]. The same ammine ligand is involved in a cyclic hydrogen bonding motif with the carboxylate group of  $\text{HADC}^-$  [N···O: 3.031(4) Å; N–H···O: 152°; graph set descriptor:  $R_2^2(6)$ ]. The chloride ions exclusively serve as acceptors for N–H···Cl<sup>-</sup> hydrogen bonds. In the case of Cl1, there are eight short contacts with N···Cl distances of 3.38–3.44 Å, while there are only six such distances for Cl2 with a larger range of 3.27–3.63 Å. Bearing in mind that Etter's hydrogen bond rules were originally formulated for organic compounds [78], it is interesting to note that the hydrogen bonding scheme observed in **2** also agrees with Etter's third hydrogen bond rule. Thus, the groups with strong relative donor strength (*i. e.* COOH and H<sub>2</sub>O) preferentially form hydrogen bonds to those with strong relative acceptor strength (*i. e.* H<sub>2</sub>O and COO<sup>-</sup>, respectively).

Upon standing in the mother liquor at room temperature (see Experimental Section), needle-shaped crystals of **2** vanish, while block-shaped crystals of **3** appear (Fig. 5a). The conversion of needles to blocks

was visually complete after approximately one month. A preliminary single-crystal X-ray analysis of one of the block-shaped crystals of **3** revealed the composition  $[\text{Co}(\text{NH}_3)_6](\text{HADC})(\text{ADC})$ , which was supported by elemental analysis. We should note that the microanalysis results show slight deviations from the expected values, indicating the presence of a minor impurity in the bulk sample, possibly resulting from an incomplete conversion of **2** into **3**. Comparison of the PXRD patterns of the crystalline bulk samples of **2** and **3**, however, shows that no significant traces of **2** are detectable in the bulk material of **3** (Fig. 3). In the crystal structure,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $\text{ADC}^{2-}$  ions form a three-dimensional hydrogen-bonded network with an open channel structure. These channels accommodate modulated  $C_2^2(7)$  hydrogen-bonded chains of  $\text{HADC}^-$  ions with the carboxylic groups in *syn*-conformation (Scheme 2), similar to those in  $\text{NH}_4(\text{HADC})$  (CSD refcode: AMHACY) [52]. Interestingly,  $[\text{Zn}(\text{H}_2\text{O})_6](\text{HADC})_2 \cdot 2\text{H}_2\text{O}$  (CSD refcode: HACYZN) [54] as well as the isomorphous Mg(II) (CSD refcode: MOYTAV) [59] and Ni(II) (CSD refcode: ASAXAU) [69] derivatives contain hydrogen-bonded tapes of  $\text{HADC}^-$  ions with carboxylic groups in *anti*-conformation. In  $[\text{C}(\text{NH}_2)_3](\text{HADC})$  (CSD refcode: VOTMEW) [57], the  $\text{HADC}^-$  ions form hydrogen-bonded tapes with carboxylic groups in *syn*- and *anti*-conformation in an alternating fashion. Adequate elucidation of the incommensurately modulated crystal structure of **3** is beyond the scope of this work and will be the subject of a more detailed crystallographic study. It is interesting to note that **2** is formed initially. This suggests that the for-

mation of **2** is kinetically preferred. The replacement of needle-shaped crystals of **2** by block-shaped crystals of **3** in the solution after a period of time

(a)



(b)

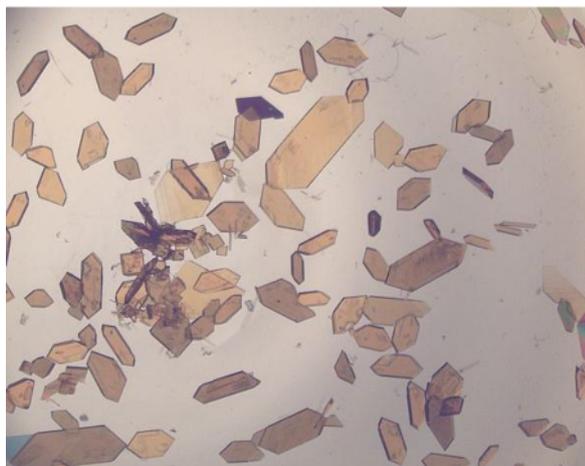
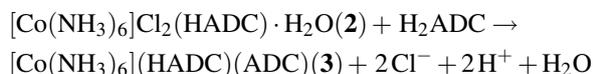


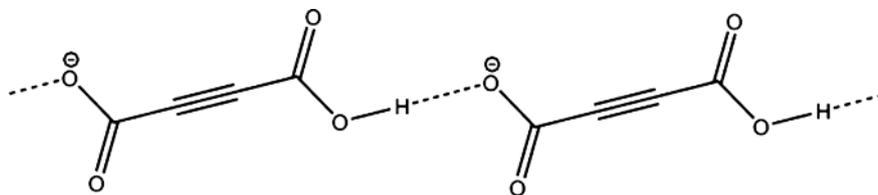
Fig. 5. (a) Microscope image of needle-shaped crystals of **2** and subsequently formed block-shaped crystals of **3** in the mother liquor after nine days; (b) plate-shaped crystals of **4**.

indicates that **3** is thermodynamically more stable than **2**. Interestingly, the transformation is associated with elimination of chloride ions from the crystalline phase:



It is reasonable to assume that the formation of strong interanion  $\text{O}-\text{H} \cdots \text{O}^-$  hydrogen bonds between  $\text{HADC}^-$  ions contributes to the factors that drive the conversion of **2** into **3**, since  $\text{N}-\text{H} \cdots \text{Cl}^-$  hydrogen bonds are generally considered to be weaker than those of the  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  type [79]. Release of chloride ions into the mother liquor (*i. e.* resolution) thus appears to be favored during the conversion of **2** into **3**.

As indicated by the formula  $[\text{Co}(\text{NH}_3)_6](\text{HADC})(\text{ADC})$ , compound **3** formally represents a water-free derivative of the dihydrate **1**. In the hope of obtaining **1** from **3** by addition of water, we subjected **3** to a simple re-crystallization experiment using water as solvent. However, to our surprise, dissolving **3** in water at  $100^\circ\text{C}$  and subsequent cooling led to plate-shaped crystals of **4** (Fig. 5b) instead of the anticipated **1**. The composition of **4** was unambiguously confirmed by single-crystal X-ray analysis to be  $[\text{Co}(\text{NH}_3)_6]_2(\text{ADC})_3 \cdot 3\text{H}_2\text{O}$ . The crystal structure of **4** contains one crystallographically independent cation and two crystallographically independent half-cations of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , the latter residing at crystallographic centers of symmetry. The three completed cations are shown in Fig. 6, together with the three unique  $\text{ADC}^{2-}$  anions and the three unique water molecules. The asymmetric unit of **4** thus comprises one formula unit ( $Z' = 1$ ). Table 1 lists bond lengths and angles for the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ions. As for **1** and **2**, bond lengths and angles at  $\text{Co}(\text{III})$  are as expected, showing only slight deviations from the regular octahedral structure. Molecular geometry parameters of  $\text{ADC}^{2-}$  are also



Scheme 2. Chemical diagram of a  $\text{C}_2^2(7)$  hydrogen-bonded chain of  $\text{HADC}^-$  ions in **3**.

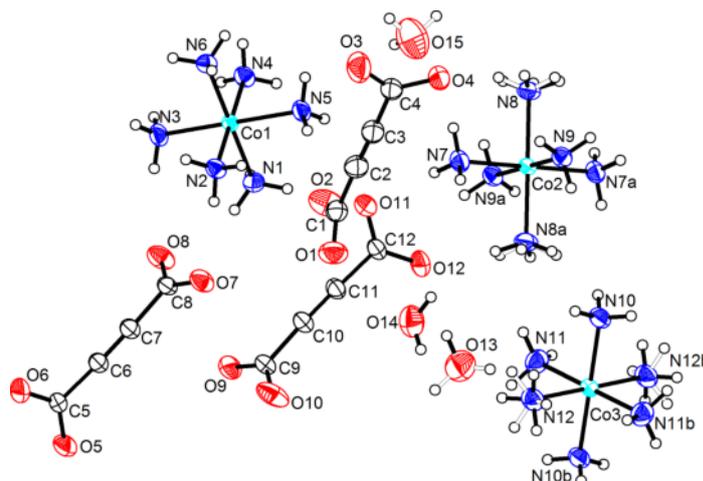


Fig. 6. Displacement ellipsoid plot (50% probability level) of **4**, showing the completed crystallographically independent half-cations around Co2 and Co3. Hydrogen atoms are represented by small spheres of arbitrary radii. Disorder of hydrogen atoms is illustrated with empty bonds. Symmetry codes: (a)  $1-x, 1-y, -z$ ; (b)  $2-x, -y, -z$ .

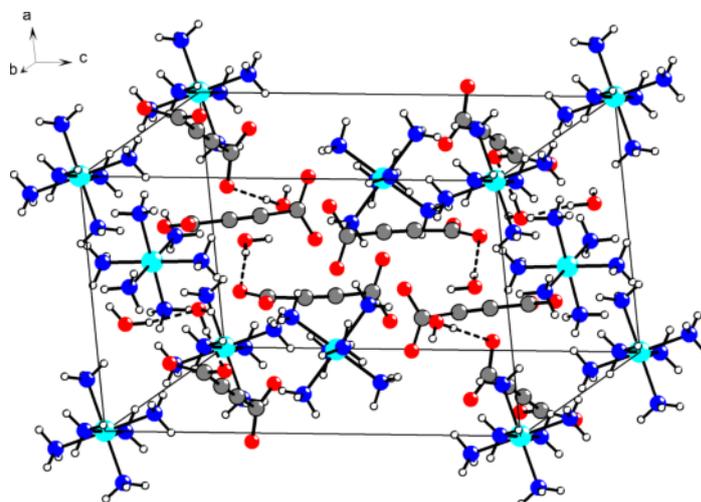


Fig. 7. (color online). View of the crystal structure of **4**, showing the triclinic unit cell. O–H...O hydrogen bonds are represented by dashed lines. For the sake of clarity, N–H...O hydrogen bonds and disorder of ammine and water hydrogen atoms are omitted. Color scheme: grey, carbon; blue, nitrogen; red, oxygen; turquoise, cobalt; white, hydrogen.

within the expected ranges. C–O bond lengths vary between 1.24–1.26 Å. The dihedral angles between the carboxylate groups are 77.8(1), 82.0(1) and 86.6(1)° in the three distinct ADC<sup>2-</sup> anions. The C1–C2, C3–C4, C5–C6, C7–C8, C9–C10, and C11–C12 bonds exhibit bond lengths of 1.46–1.47 Å. As in **1**, the C2–C3, C6–C7 and C10–C11 bonds are significantly shorter at 1.1945(16), 1.2020(11) and 1.2001(11) Å as expected for carbon–carbon triple bonds. Consis-

tently, the bond angles at C2, C3, C6, C7, C10 and C11 [177.1(1)–177.9(1)°] show only minor deviations from linearity. Figure 7 depicts the crystal structure of **4**, showing the triclinic unit cell. In the crystal structure, Co3 atoms occupy inversion centers at (0,0,0), while Co2 atoms populate inversion centers at  $(\frac{1}{2}, \frac{1}{2}, 0)$ . Co1 is located on a general position. Each  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation is surrounded by six other  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cations (Co...Co distances: 6.8–7.8 Å)

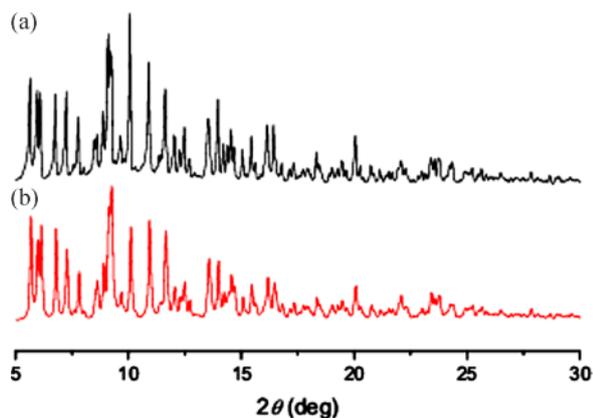
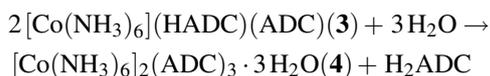


Fig. 8. (a) Experimental PXR pattern for bulk material of **4**, and (b) theoretical pattern calculated from the single-crystal structure.

forming distorted octahedra. The interstitial volume is filled by an intricate three-dimensional network of  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds with typical  $\text{O}\cdots\text{O}$  (2.77–3.21 Å) and  $\text{N}\cdots\text{O}$  (2.89–3.50 Å) distances. As for **1** and **2**, the shortest hydrogen bond distances in **4** do not involve the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cations, but rather the water molecules and the  $\text{ADC}^{2-}$  ions [ $\text{O}3\cdots\text{O}15$  2.774(2) Å,  $\text{O}13\cdots\text{O}15$  2.786(2) Å]. The hydrogen atoms attached to the water molecule O13 and O15 and the ammine ligands N8 and N12 are disordered, as illustrated in Fig. 6, but with retention of the hydrogen bonds. PXR analysis confirmed that the single-crystal of **4** studied was representative of the bulk sample (Fig. 8), revealing that crystallization of **3** from hot water affords exclusively **4**, with the elimination of  $\text{H}_2\text{ADC}$  from the crystalline phase:



As for the transformation of **2** to **3**, hydrogen bonding interactions in the solid state are likely to be important factors in promoting the formation of **4** from **3**.

## Conclusion

The crystal structure of  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC}) \cdot 2\text{H}_2\text{O}$  (**1**) has been revisited and revised. It does not contain the elusive  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  cation, but  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cations. Attempts to reproduce the crystallization of **1** only led to previously reported needle-shaped crystals of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{HADC}) \cdot \text{H}_2\text{O}$  (**2**), which upon standing in the mother liquor over sev-

eral weeks at ambient temperature were replaced by block-shaped crystals of previously unknown  $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC})$  (**3**) with the elimination of chloride ions from the solid phase. The transformation indicates that **3** is thermodynamically more stable than **2**. Compound **3** is only slightly soluble in water at ambient temperature, but dissolves in hot water. Upon cooling, exclusively plate-shaped crystals of  $[\text{Co}(\text{NH}_3)_6]_2(\text{ADC})_3 \cdot 3\text{H}_2\text{O}$  (**4**) precipitated from the solution, as confirmed by elemental analysis and PXR, with the elimination of  $\text{H}_2\text{ADC}$  from the solid phase. The conversions of **2** to **3** and **3** to **4** both illustrate the influence of crystal forces, such as different types of hydrogen bonds, in driving transformations in these systems.

## Experimental Section

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (reinst, Merck, Germany) and  $\text{H}_2\text{ADC}$  (> 98%, Fluka, Switzerland) were purchased as indicated in parentheses and used as received. Elemental analyses were carried out by Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany. IR spectra were recorded on a Perkin Elmer Spektrum One IR spectrometer with a resolution of  $1\text{ cm}^{-1}$ , using attenuated total reflection (ATR) sampling technique and a background correction (abbreviations: s = strong, m = medium, w = weak, b = broad).

### Preparation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{HADC}) \cdot \text{H}_2\text{O}$ (**2**)

A solution of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (250 mg, 0.935 mmol) in 5 mL of water was added dropwise to a stirred solution of  $\text{H}_2\text{ADC}$  (213 mg, 1.870 mmol) in 5 mL of water. An initially formed precipitate was removed by filtration, and the resulting clear orange solution was left at room temperature. After four days, orange needle-shaped crystals of **2** were collected and dried on a filter paper. Yield: 80 mg (0.220 mmol, 24%). – Anal. for  $\text{C}_4\text{H}_{21}\text{N}_6\text{O}_5\text{Cl}_2\text{Co}$ : calcd. C 13.23, H 5.83, N 23.15%; found C 13.29, H 5.89, N 23.05%. – IR(ATR)  $\tilde{\nu}$  = 3207(m,b), 3124(s,b), 1696(m), 1682(m), 1607(m), 1538(s), 1367(s), 1343(s), 1337(s), 1324(s), 1276(s), 1002(m), 872(m), 843(m)  $\text{cm}^{-1}$ .

### Preparation of $[\text{Co}(\text{NH}_3)_6](\text{ADC})(\text{HADC})$ (**3**)

The procedure was analogous to the preparation of **2**. However, the needle-shaped crystals of **2** first obtained were not removed from the mother liquor but allowed to remain in the solution at room temperature. After several days, the needle-shaped crystals started to disappear, while block-shaped crystals started to grow. After *ca.* one month, when needle-shaped crystals in the crystallization sample could no longer be identified, block-shaped orange crystals of **3**

were collected and dried on a filter paper. Yield: 70 mg (0.181 mmol, 19%). – Anal. for  $\text{C}_8\text{H}_{19}\text{N}_6\text{O}_8\text{Co}$ : calcd. C 24.88, H 4.96, N 21.76%, found C 24.12, H 4.87, 22.12%. – IR(ATR)  $\tilde{\nu} = 3220(\text{m,b}), 3097(\text{m,b}), 1599(\text{m}), 1553(\text{s}), 1339(\text{s}), 1317(\text{s}), 991(\text{w}), 871(\text{m}), 858(\text{m}), 835(\text{m}), 815(\text{w}), 789(\text{w}), 774(\text{s}), 667(\text{s}) \text{ cm}^{-1}$ .

Alternatively, in a direct synthesis, a solution of  $\text{H}_2\text{ADC}$  (114 mg, 1 mmol) in 5 mL of water was slowly added to 5 mL of a saturated solution of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in water. After one day at ambient temperature, a precipitate formed and was removed by filtration. The resulting clear filtrate was placed in a refrigerator at approximately  $6^\circ\text{C}$ . After several days, orange crystals of **3** precipitated.

#### Preparation of $[\text{Co}(\text{NH}_3)_6]_2(\text{ADC})_3 \cdot 3 \text{H}_2\text{O}$ (**4**)

Compound **3** (30 mg, 0.078 mmol) was dissolved in 4 mL of deionized water at  $100^\circ\text{C}$ . After slow cooling to room temperature, plate-shaped orange crystals of **4** precipitated. The crystals were collected and dried on a filter paper. Yield: 20 mg (0.028 mmol, 36%). – Anal. for  $\text{C}_{12}\text{H}_{42}\text{N}_{12}\text{O}_{15}\text{Co}_2$ : calcd. C 20.23, H 5.94, N 23.59%; found C 20.26, H 5.80, N 23.41%. – IR(ATR)  $\tilde{\nu} = 3190(\text{m,b}), 3107(\text{m,b}), 1601(\text{m}),$

$1548(\text{s}), 1318(\text{s}), 1054(\text{w}), 998(\text{m}), 878(\text{m}), 837(\text{w}), 782(\text{m}), 773(\text{m}), 672(\text{m}) \text{ cm}^{-1}$ .

Alternatively, a solution of  $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$  (2.530 g, 11.93 mmol) in 10 mL of water was added dropwise to a solution of  $\text{H}_2\text{ADC}$  (570 mg, 5 mmol) in 10 mL of water, until a pH of approximately 5.5 was reached. The resulting gel was carefully layered with 10 mL of a saturated aqueous solution of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ . After two days orange crystals of **4** grew at the phase boundary. These crystals were isolated, washed with water and dried in air.

#### Single-crystal X-ray analyses

The preparation of crystals of **1** suitable for single-crystal X-ray diffraction is described in [69]. It could not be reproduced in this work, so the crystal structure of **1** was re-refined using the X-ray intensity data originally attributed to  $[\text{Co}(\text{H}_2\text{O})_6](\text{ADC})(\text{HADC}) \cdot 2 \text{H}_2\text{O}$  [69], which had been collected at room temperature on a Stoe IPDS diffractometer, using Ge-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were rescaled with SADABS [80] for the present study. Crystals of **4** suitable for single-crystal X-ray diffraction were obtained as described above. The corresponding

Table 2. Crystal structure data for **1** and **4** at room temperature.

	<b>1</b>	<b>4</b>
Empirical formula	$\text{C}_8\text{H}_{23}\text{N}_6\text{O}_{10}\text{Co}$	$\text{C}_{12}\text{H}_{42}\text{N}_{12}\text{O}_{15}\text{Co}_2$
$M_r$	422.25	712.43
Crystal size, mm <sup>3</sup>	$0.40 \times 0.20 \times 0.05$	$0.47 \times 0.40 \times 0.22$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
$a$ , Å	7.0915(8)	9.443(1)
$b$ , Å	16.908(2)	10.4599(11)
$c$ , Å	13.7001(17)	14.8326(15)
$\alpha$ , deg	90	104.888(2)
$\beta$ , deg	97.504(14)	93.588(2)
$\gamma$ , deg	90	90.525(2)
$V$ , Å <sup>3</sup>	1628.7(3)	1412.6(3)
$Z$	4	2
$D_{\text{calcd.}}$ , g cm <sup>-3</sup>	1.72	1.68
$\mu(\text{MoK}\alpha)$ , cm <sup>-1</sup>	1.1	1.3
$F(000)$ , e	880	744
$hkl$ range	$\pm 8, \pm 22, \pm 18$	$\pm 15, \pm 17, \pm 24$
$\theta_{\text{max}}$ , deg	28.16	36.55
Refl. measured	15424	53770
Refl. unique	3685	13461
$R_{\text{int}}$	0.1109	0.0165
Param. refined	245	411
$R1/wR2^{\text{a,b}}$ [ $F^2 > 2\sigma(F^2)$ ]	0.0555/0.1112	0.0266/0.0744
$R1/wR2^{\text{a,b}}$ (all reflections)	0.1087/0.1326	0.0332/0.0795
GoF ( $F^2$ ) <sup>c</sup>	1.023	1.013
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>-3</sup>	0.51/−0.76	0.41/−0.91

<sup>a</sup>  $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ ; <sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ; <sup>c</sup>  $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

X-ray intensity data were measured at room temperature on a Bruker AXS APEX II diffractometer, using  $\text{MoK}\alpha$  radiation from a FR591 rotating anode with an Incoatec Helios multilayer mirror. The data collection was carried out with the APEX2 software [81]. The data were integrated with SAINT [82], corrected for absorption using Gaussian numerical integration based on the crystal faces and scaled with SADABS, using multiple-scanned reflections. The crystal structure was solved by Direct Methods using SHELXS-97 [83].

The crystal structures of **1** and **4** were refined by full-matrix least-squares refinements on  $F^2$  with SHELXL-2013 [83]. SHELXLE was used as a graphical user interface for the inspection of difference electron density maps during the structure refinements [84]. Anisotropic displacement parameters were introduced for all non-hydrogen atoms. The ammine and carboxyl hydrogen atoms were placed at geometrically calculated positions (N–H: 0.89 Å, O–H: 0.82 Å) and refined with the appropriate riding model, allowing rotation of the rigid group about the respective Co–N and C–O bonds, with initial torsion angles determined from difference Fourier syntheses.  $U_{\text{iso}}(\text{H})$  values were set 1.5 times  $U_{\text{eq}}(\text{N}, \text{O})$  for ammine ligands and carboxy groups and 1.2 times  $U_{\text{eq}}(\text{O})$  for water molecules. In **4**, rotational disorder of the hydrogen atoms bonded to N8 and N12 was observed. The disorder was described by a split model. The ratio between the occupancies of the disorder sites was each refined by means of a free variable to yield 0.53(2) : 0.47(2) for the hydrogen atoms attached to N8 and 0.60(2) : 0.40(2) for those attached to N12. The water hydrogen atoms were located in difference Fourier maps. The water O–H bond lengths were restrained to a target value of 0.82(2) Å, and similar distance restraints with a standard uncertainty of 0.04 Å were applied to the intramolecular H–H distances. One of the water hy-

drogen atoms bonded to O13 and O15 in **4** was found to be disordered over two positions in each case. This was also described by split models with a site occupancy factor of 0.5 for the disorder sites. Relevant crystallographic data and refinement details for **1** and **4** are listed in Table 2. Structure representations were drawn with DIAMOND [85].

CCDC 963924 and 963925 contain the supplementary crystallographic data for **1** and **4**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Powder X-ray diffraction

PXRD data for bulk material of **2–4** were recorded at room temperature in Debye-Scherrer geometry on a Stoe Stadi P system with a linear position sensitive detector and focused  $\text{MoK}\alpha_1$  radiation ( $\lambda = 0.70932$  Å) from a curved Ge(111) monochromator (step size in  $2\theta = 0.03^\circ$ ). Powder samples of **2–4** were prepared by grinding crystals in an agate mortar. The capillary samples (inner diameter = 0.5 mm) were rotated during the measurements. The WINXPOW software was used to operate the diffractometer [86]. Theoretical powder patterns were calculated from the single-crystal data with MERCURY [87, 88]. Single-crystal data for **2** at room temperature were taken from reference [69] (CCDC 745361).

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