



Complexes of nickel(II) and copper(II) with 1,2,4-triazole-3-carboxylic acid and of cobalt(III) with 3-amino-1,2,4-triazole-5-carboxylic acid

Feng-Yi Liu, Dong-Mei Zhou, Xiao-Lan Zhao and Jun-Feng Kou*

College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, People's Republic of China. *Correspondence e-mail: kjf416@163.com

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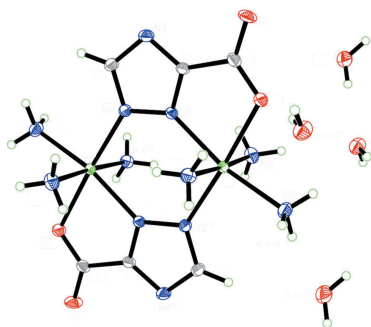
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Because of their versatile coordination modes and strong coordination ability for metals, triazole ligands can provide a wide range of possibilities for the construction of metal-organic frameworks. Three transition-metal complexes, namely bis(μ -1,2,4-triazol-4-ide-3-carboxylato)- $\kappa^3 N^2, O: N^1; \kappa^3 N^1: N^2, O$ -bis[triamminenickel(II)] tetrahydrate, $[\text{Ni}_2(\text{C}_3\text{HN}_3\text{O}_2)_2(\text{NH}_3)_6] \cdot 4\text{H}_2\text{O}$, (I), *catena*-poly[[[diamminediaquacopper(II)]- μ -1,2,4-triazol-4-ide-3-carboxylato- $\kappa^3 N^1: N^4, O$ -[diamminecopper(II)]- μ -1,2,4-triazol-4-ide-3-carboxylato- $\kappa^3 N^4, O: N^1$] dihydrate], $\{[\text{Cu}_2(\text{C}_3\text{HN}_3\text{O}_2)_2(\text{NH}_3)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$, (II), (μ -5-amino-1,2,4-triazol-1-ide-3-carboxylato- $\kappa^2 N^1: N^2$)di- μ -hydroxido- $\kappa^4 O: O$ -bis[triammincobalt(III)] nitrate hydroxide trihydrate, $[\text{Co}_2(\text{C}_3\text{H}_2\text{N}_4\text{O}_2)(\text{OH})_2(\text{NH}_3)_6](\text{NO}_3)(\text{OH}) \cdot 3\text{H}_2\text{O}$, (III), with different structural forms have been prepared by the reaction of transition metal salts, *i.e.* NiCl_2 , CuCl_2 and $\text{Co}(\text{NO}_3)_2$, with 1,2,4-triazole-3-carboxylic acid or 3-amino-1,2,4-triazole-5-carboxylic acid hemihydrate in aqueous ammonia at room temperature. Compound (I) is a dinuclear complex. Extensive O—H...O, O—H...N and N—H...O hydrogen bonds and π - π stacking interactions between the centroids of the triazole rings contribute to the formation of the three-dimensional supramolecular structure. Compound (II) exhibits a one-dimensional chain structure, with O—H...O hydrogen bonds and weak O—H...N, N—H...O and C—H...O hydrogen bonds linking anions and lattice water molecules into the three-dimensional supramolecular structure. Compared with compound (I), compound (III) is a structurally different dinuclear complex. Extensive N—H...O, N—H...N, O—H...N and O—H...O hydrogen bonding occurs in the structure, leading to the formation of the three-dimensional supramolecular structure.

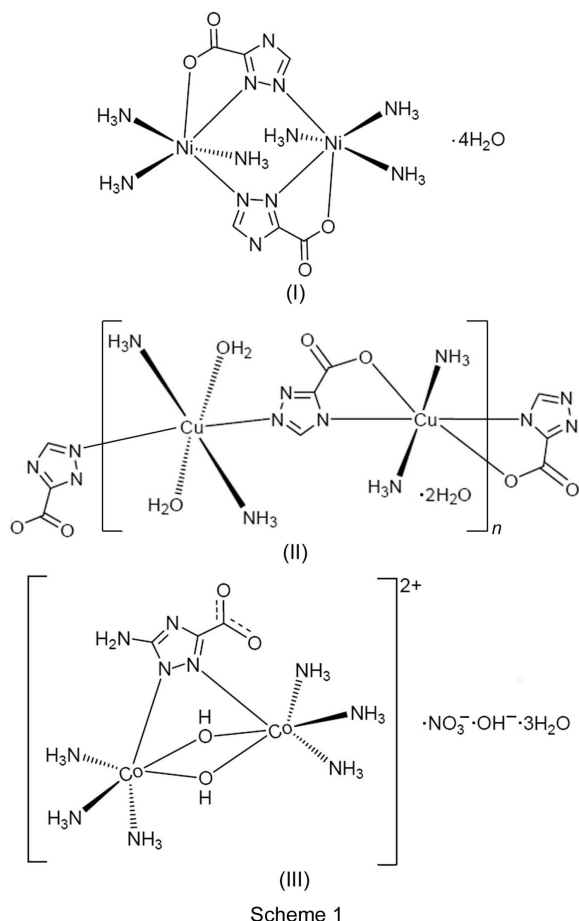
1. Introduction

The design and synthesis of coordination polymers are of great interest aesthetically and for practical applications in crystal engineering and supramolecular chemistry (Yaghi *et al.*, 2003). Since many factors, including the coordination requirements of the central metal atom and features of the organic ligand, solvent, temperature, ratio of reactants, reaction time and pH, could influence self-assembly, prediction of the resultant crystal structures of a given metal-ligand system is still very difficult. The experiment-feedback-experiment exploration mode still dominates the field of crystal engineering and continually enriches and deepens our comprehension of coordination-driven self-assembly (Han *et al.*, 2014).

Because of the versatile coordination modes and strong coordination ability of deprotonated azolate ligands for transition-metal ions (Zhang *et al.*, 2006), metal-azolate frameworks consist of a unique type of coordination polymer which is beneficial for the control of structure formation. Recent years have witnessed increasing interest in metal-



1,2,4-triazolates (Yang *et al.*, 2009; Demessence *et al.*, 2009; Ouellette *et al.*, 2011; Aromí *et al.*, 2011). Most of the triazoles used in coordination polymers are symmetric (Haasnoot *et al.*, 2000; Adriaanse *et al.*, 2009) and only a few reports are known concerning metal complexes with asymmetric triazoles (Su *et al.*, 2004; Kou *et al.*, 2009; Zhang *et al.*, 2005; Zhang, Qi *et al.*, 2011; Zhang, Wei *et al.*, 2011; Lin *et al.*, 2012). The asymmetric nature of triazoles may have a fundamental structural influence on coordination polymers. In this paper, we report the synthesis and crystal structures of three transition-metal complexes with two asymmetric ligands, *viz.* 1,2,4-triazole-3-carboxylic acid (tzCOOH) and 3-amino-1,2,4-triazole-5-carboxylic acid (atzCOOH), namely $[\text{Ni}_2(\text{tzCOO})_2(\text{NH}_3)_6] \cdot 4\text{H}_2\text{O}$, (I), $[\{\text{Cu}_2(\text{tzCOO})_2(\text{NH}_3)_4(\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}]_n$, (II), and $[\text{Co}_2(\text{atzCOO})(\text{OH})_2(\text{NH}_3)_6](\text{NO}_3)(\text{OH}) \cdot 3\text{H}_2\text{O}$. We chose these two asymmetric ligands because they both display versatile coordination modes upon binding to metals. The carboxylate group can act in a terminal or bridging coordination mode, and can also be used as a monodentate or bidentate coordination group. The amino group in atzCOOH can act as an additional monodentate coordination functional group.

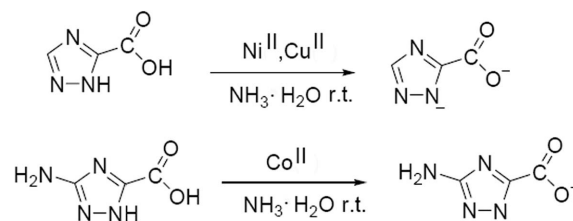


2. Experimental

2.1. Synthesis and crystallization

For the synthesis of (I), a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (118.8 mg, 0.500 mmol) in aqueous ammonia (25%, 4 ml) was mixed with

an aqueous ammonia solution (4 ml) of tzCOOH (56.0 mg, 0.500 mmol). The resulting mixture was allowed to evaporate for one week to give green crystals of (I) (yield 80%, based on the ligand). Analysis calculated for $\text{C}_6\text{H}_{28}\text{N}_{12}\text{Ni}_2\text{O}_8$: C 14.03, H 5.49, N 32.72%; found: C 14.01, H 5.48, N 32.74%. IR (KBr, pellet, ν , cm^{-1}): 3443 (s), 1623 (s), 1539 (w), 1474 (s), 1384 (s), 1310 (s), 1100 (w), 833 (w), 535 (w).



Scheme 2

Compound (II) was prepared by a procedure analogous to that used for the preparation of (I), using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (85.2 mg, 0.5 mmol) or CuAc_2 (0.5 mmol, 99.8 mg; Ac is acetate) instead of NiCl_2 to give blue blocks of (II) (yield 75%, based on the ligand). Analysis calculated for $\text{C}_3\text{H}_{11}\text{CuN}_5\text{O}_4$: C 14.73, H 4.53, N 28.62%; found: C 14.71, H 4.51, N 28.63%. IR (KBr pellet, ν , cm^{-1}): 3373 (s), 1608 (s), 1508 (s), 1452 (s), 1387 (s), 1329 (s), 1298 (s), 1187 (m), 1147 (m), 1060 (m), 1027 (m), 829 (s), 670 (s).

For the synthesis of complex (III), a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (145.5 mg, 0.500 mmol) in aqueous ammonia (25%, 2 ml) was mixed with an aqueous ammonia solution (4 ml) of atzCOOH (64.0 mg, 0.500 mmol). The resulting clear solution was allowed to evaporate slowly for one week to generate red crystals of (III) (yield 50%, based on Co). Analysis calculated for $\text{C}_3\text{H}_{29}\text{Co}_2\text{N}_{11}\text{O}_{11}$: C 7.02, H 5.70, N 30.02%; found: C 7.01, H 5.72, N 29.98%. IR (KBr pellet, ν , cm^{-1}): 3405 (s), 1671 (s), 1462 (s), 1364 (s), 1291 (s), 1198 (m), 1148 (m), 1055 (w), 890 (w), 834 (m), 663 (s), 581 (m).

2.2. Refinement

Crystal data, data collection and structure refinement details for (I)–(III) are summarized in Table 1. H atoms attached to C atoms were fixed geometrically and allowed to ride on the corresponding non-H atom, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms. The positions of the methyl H atoms were optimized rotationally. The H atoms of complexes (I) and (III) were restrained with $\text{N}-\text{H} = 0.81\text{--}0.91 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The H atoms of complex (II) were constrained with $\text{N}-\text{H} = 0.89 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The water H atoms of (I)–(III) were located from difference Fourier maps and restrained with $\text{O}-\text{H} = 0.73\text{--}0.85 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

3. Results and discussion

The three complexes reported here were prepared by the reaction of tzCOOH or atzCOOH with the corresponding divalent metal salts in aqueous ammonia solution at room temperature. In the three crystal structures, both ligands are

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$[\text{Ni}_2(\text{C}_3\text{HN}_3\text{O}_2)_2(\text{NH}_3)_6]\cdot 4\text{H}_2\text{O}$	$[\text{Cu}(\text{C}_3\text{HN}_3\text{O}_2)(\text{NH}_3)_2(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$	$[\text{Co}_2(\text{C}_3\text{H}_2\text{N}_4\text{O}_2)(\text{OH})_2(\text{NH}_3)_6]\cdot (\text{NO}_3)(\text{OH})\cdot 3\text{H}_2\text{O}$
M_r	513.78	244.72	513.23
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Temperature (K)	293	293	293
a, b, c (Å)	7.1226 (14), 9.0134 (18), 9.1203 (18)	7.2183 (14), 7.4079 (15), 9.887 (2)	7.0765 (14), 12.676 (3), 20.591 (4)
α, β, γ (°)	103.16 (3), 107.48 (3), 106.69 (3)	72.45 (3), 68.82 (3), 62.74 (3)	90, 98.70 (3), 90
V (Å ³)	502.4 (2)	432.3 (2)	1825.8 (6)
Z	1	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	1.94	2.52	1.89
Crystal size (mm)	0.30 × 0.27 × 0.25	0.31 × 0.28 × 0.26	0.31 × 0.28 × 0.26
Data collection			
Diffractometer	Rigaku MM007-HF CCD (Saturn 724+)	Rigaku MM007-HF CCD (Saturn 724+)	Rigaku MM007-HF CCD (Saturn 724+)
Absorption correction	Multi-scan (SADABS; Sheldrick, 1996)	Multi-scan (SADABS; Sheldrick, 1996)	Multi-scan (SADABS; Sheldrick, 1996)
$T_{\text{min}}, T_{\text{max}}$	0.565, 0.616	0.509, 0.560	0.561, 0.611
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3780, 1767, 1641	3353, 1500, 1248	13577, 3212, 2940
R_{int}	0.034	0.055	0.043
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.595	0.594	0.595
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.071, 1.06	0.052, 0.145, 1.04	0.031, 0.084, 1.06
No. of reflections	1767	1500	3212
No. of parameters	166	123	332
No. of restraints	15	0	31
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	Only H-atom coordinates refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.34	1.40, -0.67	0.53, -0.50

Computer programs: *CrystalStructure* (Rigaku/MSC, 2006), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *SHELXTL* (Sheldrick, 2008).

dianionic, generated by dissolution in aqueous ammonia solution (Scheme 2). Due to the easy formation of precipitates, it is very difficult to obtain crystals of complexes by direct reaction of the transition metal salt with the corresponding ligands. However, by using an ammonia solution of the transition metal, we have successfully obtained crystals of three transition-metal complexes with Ni²⁺, Cu²⁺ and Co³⁺.

Displacement ellipsoid plots for complexes (I), (II) and (III) are shown in Figs. 1, 2 and 3, respectively. The dinickel complex (I) crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit consists of one crystallographically independent Ni²⁺ atom, one tzCOO²⁻ ligand, three ammonia ligands and two solvent water molecules. As shown in Fig. 1, the complex is a binuclear molecule with tzCOO²⁻ acting as a tridentate bridging ligand between the two Ni²⁺ ions in a μ -*O,N²:N¹* fashion. Each Ni²⁺ atom is bound to two donor atoms (N1 and O2) of one tzCOO²⁻ ligand, one donor atom (N2) of

another tzCOO²⁻ ligand and three ammonia ligands, forming an almost regular octahedral coordination geometry (Table 2).

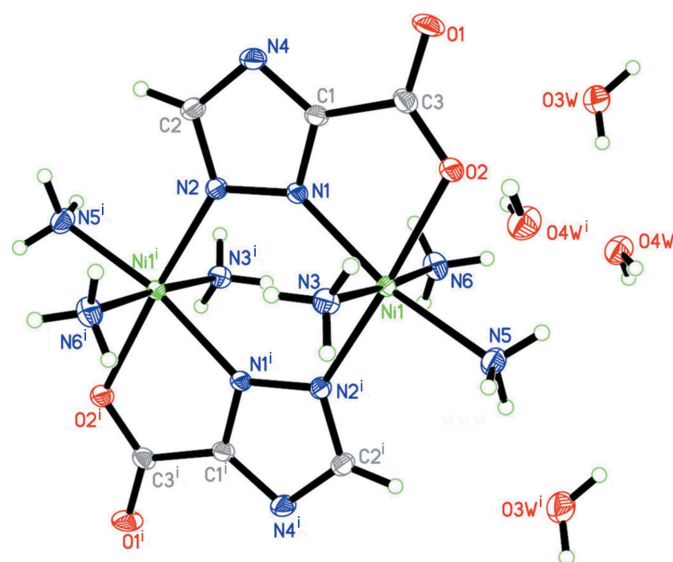
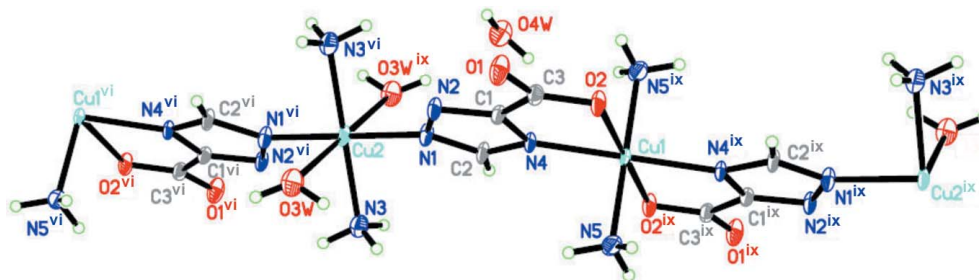


Figure 1
The molecular structure of complex (I), showing the atom labelling and 50% probability displacement ellipsoids. [Symmetry code: (i) $-x, -y + 1, -z$.]

Table 2
Selected bond lengths (Å) for (I).

Ni1—N2 ⁱ	2.0745 (19)	Ni1—N5	2.110 (2)
Ni1—N1	2.0825 (18)	Ni1—N6	2.114 (2)
Ni1—N3	2.106 (2)	Ni1—O2	2.1651 (18)

Symmetry code: (i) $-x, -y + 1, -z$.


Figure 2

The structure of a fragment of complex (II), showing the atom labelling and 50% probability displacement ellipsoids. [Symmetry code: (vi) $-x + 2, -y, -z$; (ix) $-x + 1, -y + 1, -z + 1$.]

Table 3

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H3B\cdots O1^{ii}$	0.83 (2)	2.20 (2)	3.010 (3)	163 (2)
$N3-H3C\cdots O4W^{iii}$	0.81 (2)	2.65 (2)	3.307 (3)	139 (2)
$N5-H5A\cdots O3W^{ii}$	0.90 (2)	2.23 (2)	3.123 (3)	168 (2)
$N5-H5C\cdots O2^{iii}$	0.86 (2)	2.47 (2)	3.286 (3)	157 (2)
$N6-H6A\cdots O3W^{iv}$	0.86 (2)	2.37 (2)	3.193 (3)	161 (3)
$N6-H6C\cdots O4W$	0.86 (2)	2.21 (2)	3.067 (3)	175 (3)
$O3W-H3WA\cdots O1^v$	0.81 (2)	2.07 (2)	2.805 (3)	151 (3)
$O3W-H3WB\cdots O4W$	0.84 (2)	1.99 (2)	2.821 (3)	177 (4)
$O4W-H4WA\cdots N4^{vi}$	0.83 (2)	1.99 (2)	2.802 (3)	168 (3)
$O4W-H4WB\cdots O2^{iii}$	0.83 (2)	1.97 (2)	2.795 (2)	169 (3)

Symmetry codes: (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + 2, -y + 2, -z + 1$; (vi) $x, y, z + 1$.

The dimeric $Ni_2(N-N)_2$ subunit for N1 and Ni1^{vi} [symmetry code: (vi) $-x, -y + 1, -z$] is formed *via* coordination of atoms N1 and N2 of the triazole group. Such a six-membered ($M-N-N$)₂ ring is common in metal-azolate complexes (Haasnoot *et al.*, 2000; Kou *et al.*, 2009; La Monica *et al.*, 1997; Yang *et al.*, 2007). Strong hydrogen bonds involving water O atoms (as donors) and water O atoms or triazole N atoms (as acceptors) from the ligand ($O3W\cdots O1^{iv}$, $O3W\cdots O4W$, $O4W\cdots N4^v$ and $O4W\cdots O2^{ii}$; see Table 3 for details) and weak hydrogen bonds between the ammonia ligands (as donors) and water or carboxylate O atoms (as acceptors) ($N3\cdots O4W^{ii}$, $N3\cdots O1^i$,

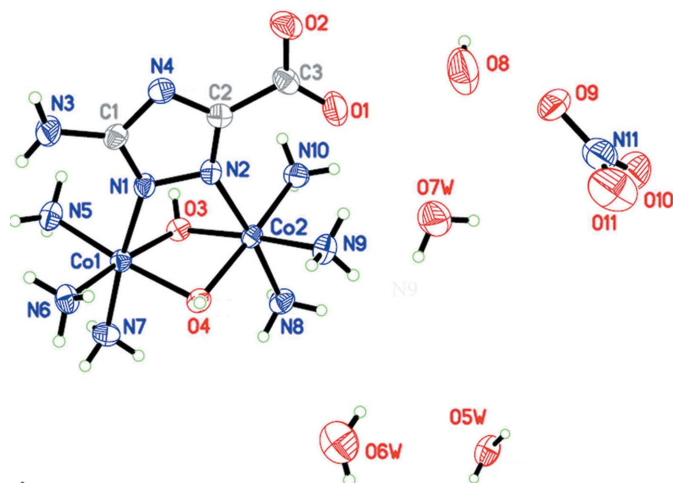
Table 4

Selected bond lengths (\AA) for (II).

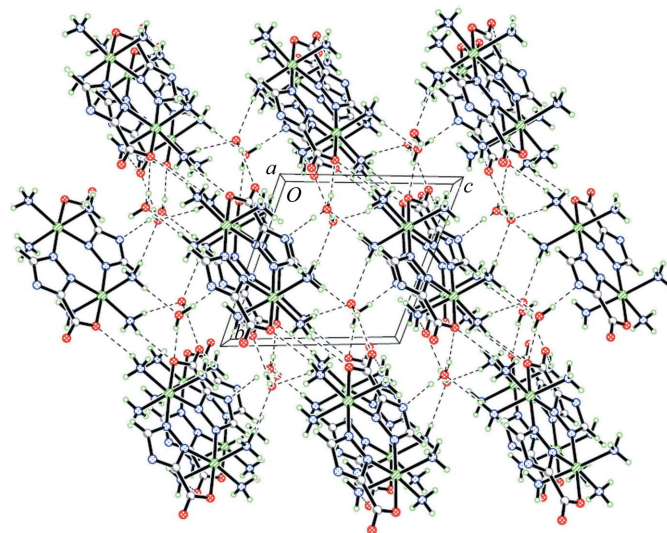
Cu1—N4	1.992 (3)	Cu2—N1	1.999 (3)
Cu1—N5	2.013 (3)	Cu2—N3	2.061 (4)
Cu1—O2	2.560 (3)	Cu2—O3W	2.574 (3)

$N5\cdots O2^{ii}$, $N5\cdots O3W^i$, $N6\cdots O3W^{iii}$ and $N6\cdots O4W$; see Table 3 for details), as well as π - π stacking interactions, with a separation of 3.6951 (10) \AA between the centroids of the triazole rings of the ligand, contribute to the formation of the three-dimensional supramolecular structure (Fig. 4).

The one-dimensional Cu^{II} coordination polymer (II) crystallizes in the monoclinic space group $P\bar{1}$. The asymmetric unit consists of two Cu^{2+} atoms, one $tzCOO^{2-}$ ligand, two ammonia ligands, one coordinated water molecule and one crystalline water molecule. As shown in Fig. 2, the Cu1 atom is bound to two N4 atoms [$N4/N4^{ix}$; symmetry code: (ix) $-x + 1, -y + 1, -z + 1$] and two O2 atoms ($O2/O2^{ix}$) of two $tzCOO^{2-}$ ligands, and to two N atoms ($N5/N5^{ix}$) from two ammonia ligands, forming an elongated octahedral coordination geometry due to a Jahn-Teller effect for the d^9 configuration (Table 4). Likewise, the Cu2 atom is coordinated by two N1 atoms [$N1/N1^{vi}$; symmetry code: (vi) $-x + 2, -y, -z$] of two triazole


Figure 3

The molecular structure of complex (III), showing the atom labelling and 50% probability displacement ellipsoids.


Figure 4

A view of the crystal packing of complex (I). Hydrogen bonds are shown as dashed lines.

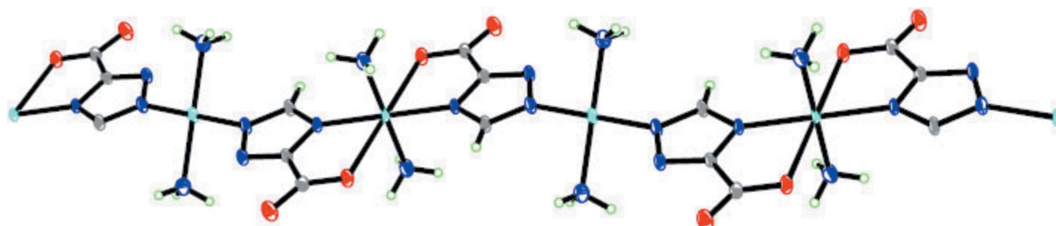


Figure 5
A view of the one-dimensional ribbon of complex (II) along the *c* axis.

Table 5
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N3—H3A···O4W ⁱ	0.89	2.27	3.115 (6)	158
N3—H3B···O2 ⁱⁱ	0.89	2.37	3.207 (5)	157
N3—H3C···O4W ⁱⁱⁱ	0.89	2.37	3.194 (5)	154
N5—H5B···O1 ^{iv}	0.89	2.49	3.057 (5)	122
N5—H5C···O1 ^v	0.89	2.25	3.106 (5)	162
O3W—H3WA···O4W ^{vi}	0.82	1.98	2.783 (6)	169
O3W—H3WB···O2 ^v	0.84	2.07	2.844 (4)	154
O4W—H4WA···O1 ^{vii}	0.83	2.00	2.608 (5)	129
O4W—H4WB···O3W ^{viii}	0.82	2.11	2.869 (5)	152
C2—H2···O4W ⁱ	0.93	2.53	3.401 (7)	156

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y, z-1$; (iii) $x+1, y, z$; (iv) $x, y+1, z$; (v) $-x+2, -y, -z+1$; (vi) $-x+2, -y, -z$; (vii) $-x+1, -y, -z+1$; (viii) $x-1, y+1, z$.

groups, two coordinated water molecules and two ammonia ligands in an elongated octahedral coordination geometry. The two Cu²⁺ atoms are bridged through the triazole N1 and N4 positions to form a one-dimensional chain along the *a* axis (Fig. 5). Compared with complex (I), although the tzCOO²⁻ ligand in complex (II) also serves as a tridentate ligand, it adopts a μ -*O,N*⁴:*N*¹ bridging mode. Moreover, weak hydrogen bonds involving the ammonia ligands or C atoms of the triazole ring (as a donor), water molecules and the carboxylate groups from the ligand (as acceptors) (N5···O1^{iv}, N5···O1^v, N3···O2ⁱⁱ, N3···O4Wⁱ and C2···O4Wⁱ; for details see Table 5) and strong hydrogen bonds involving coordinated water molecules (as donors), and carboxylate groups of the

Table 6
Selected bond lengths (Å) for (III).

Co1—O4	1.9103 (18)	Co2—O4	1.9174 (18)
Co1—N1	1.914 (2)	Co2—N9	1.922 (2)
Co1—O3	1.9261 (19)	Co2—O3	1.9231 (18)
Co1—N7	1.945 (2)	Co2—N10	1.943 (2)
Co1—N6	1.950 (2)	Co2—N8	1.947 (2)
Co1—N5	1.952 (2)	Co2—N2	1.963 (2)

tzCOO²⁻ ligand or crystalline water molecules (as acceptors) (O4W···O1^{vii}, O4W···O3W^{viii}, O3W···O4W^{vi} and O3W···O2^v; for details see Table 5) form the three dimensional supramolecular structure (Fig. 6).

The dicobalt complex (III) crystallizes in the monoclinic space group *P*2₁/*n*, the asymmetric unit consisting of two Co³⁺ atoms, one tzCOO²⁻ ligand, two hydroxide anions coordinated to Co³⁺, six ammonia ligands coordinated to Co³⁺, three crystalline water molecules, one uncoordinated hydroxide anion and one free nitrate anion (Table 6). As shown in Fig. 3, in the binuclear molecule, analogous to complex (I), each Co³⁺ ion forms an octahedral coordination geometry, binding to one of the triazole N atoms of one atzCOO²⁻ ligand, three N atoms from three ammonia molecules and two hydroxide anions. Compared with previous reports, the Co—N(triazole) bond lengths of complex (III) are similar to those of Co^{III} complexes (Ritzmann *et al.*, 2014), and deviate from the range of Co^{II}—N bond lengths (2.037–2.187 Å; Ghoshal *et al.*, 2004). The Co—O(hydroxide) bond lengths are also rather shorter

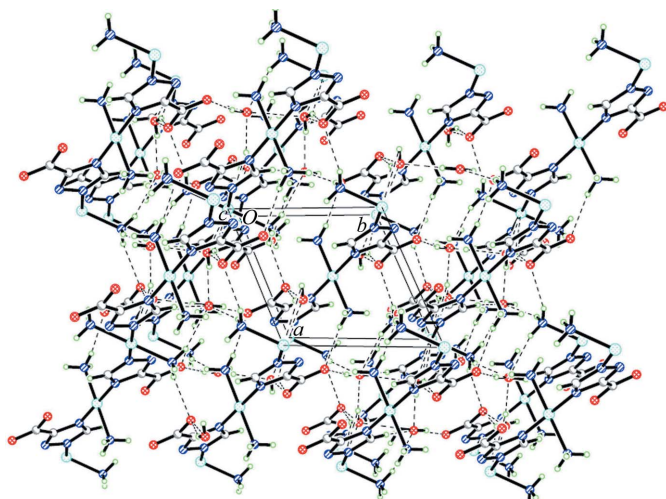


Figure 6
A view of the crystal packing of complex (II). Hydrogen bonds are shown as dashed lines.

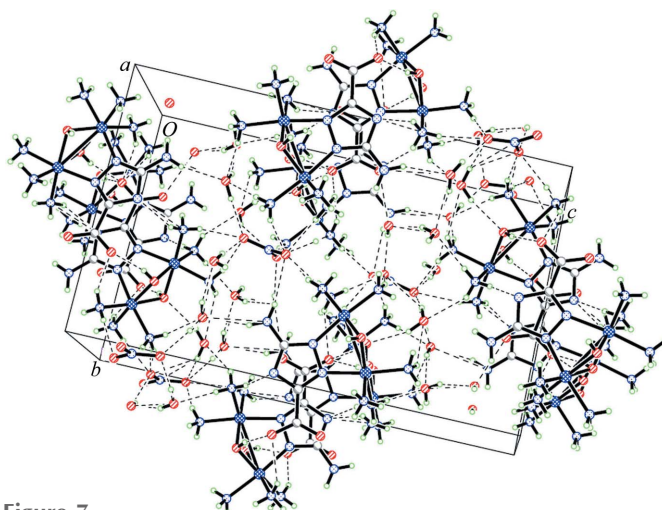


Figure 7
A view of the crystal packing of complex (III). Hydrogen bonds are shown as dashed lines.

Table 7
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N3—H3A···O5W ⁱ	0.85 (2)	2.15 (2)	2.951 (3)	158 (3)
N3—H3B···O9 ⁱⁱ	0.86 (2)	2.35 (2)	3.190 (3)	169 (3)
N5—H5A···O9 ⁱⁱ	0.87 (2)	2.19 (2)	3.039 (3)	166 (3)
N5—H5B···O2 ⁱⁱⁱ	0.88 (2)	2.56 (2)	3.344 (3)	149 (3)
N5—H5C···O11 ^{iv}	0.88 (2)	2.09 (2)	2.955 (4)	168 (3)
N6—H6A···O9 ⁱⁱ	0.86 (2)	2.09 (2)	2.922 (3)	163 (3)
N6—H6B···O2 ⁱⁱ	0.85 (2)	2.30 (2)	3.079 (3)	153 (3)
N6—H6C···O9 ^v	0.88 (2)	2.13 (2)	2.988 (3)	166 (3)
N7—H7A···O11 ^{iv}	0.85 (2)	2.12 (2)	2.929 (3)	159 (3)
N7—H7A···O7W ^{vi}	0.85 (2)	2.65 (3)	3.060 (4)	111 (3)
N7—H7B···O9 ^v	0.84 (2)	2.19 (2)	2.997 (3)	160 (3)
N7—H7B···O10 ^v	0.84 (2)	2.66 (3)	3.297 (4)	134 (3)
N7—H7C···O5W ^{vii}	0.84 (2)	2.57 (2)	3.372 (4)	161 (3)
N8—H8A···O7W ^{vi}	0.84 (2)	2.56 (3)	3.215 (4)	135 (3)
N8—H8B···O5W ^{vii}	0.87 (2)	2.16 (2)	3.016 (3)	171 (3)
N8—H8C···N11 ^{viii}	0.87 (2)	2.67 (2)	3.506 (4)	162 (3)
N8—H8C···O10 ^{viii}	0.87 (2)	2.27 (2)	3.075 (3)	154 (3)
N8—H8C···O11 ^{viii}	0.87 (2)	2.62 (2)	3.411 (4)	151 (3)
N9—H9A···N4 ⁱⁱ	0.84 (2)	2.23 (2)	2.982 (3)	148 (3)
N9—H9B···O10 ^{viii}	0.85 (2)	2.30 (2)	3.130 (3)	167 (3)
N9—H9C···O1	0.83 (2)	2.14 (2)	2.881 (3)	148 (3)
N10—H10A···O6W ^{ix}	0.86 (2)	2.23 (2)	3.083 (4)	176 (3)
N10—H10B···O7W	0.84 (2)	2.41 (2)	3.120 (4)	143 (3)
N10—H10C···N4 ⁱⁱⁱ	0.85 (2)	2.21 (2)	3.039 (3)	165 (3)
O3—H3···O2 ⁱⁱⁱ	0.78 (2)	2.18 (2)	2.952 (3)	170 (3)
O4—H4···O2 ⁱⁱ	0.81 (4)	2.15 (4)	2.947 (3)	166 (3)
O5W—H5WA···O6W ^x	0.86 (2)	2.07 (2)	2.886 (4)	157 (4)
O5W—H5WB···O10 ^{xi}	0.85 (2)	1.95 (2)	2.776 (3)	165 (4)
O6W—H6WA···O8 ^{viii}	0.83 (2)	1.94 (3)	2.746 (4)	162 (5)
O6W—H6WB···N11 ^{viii}	0.83 (2)	2.68 (3)	3.411 (4)	148 (4)
O6W—H6WB···O10 ^{viii}	0.83 (2)	1.89 (2)	2.717 (4)	174 (5)
O7W—H7WA···O3 ^{xii}	0.86 (2)	2.13 (3)	2.933 (3)	155 (5)
O7W—H7WB···N11 ^{viii}	0.89 (2)	2.56 (3)	3.353 (4)	149 (4)
O7W—H7WB···O10 ^{viii}	0.89 (2)	2.10 (3)	2.933 (4)	158 (4)
O7W—H7WB···O11 ^{viii}	0.89 (2)	2.39 (4)	3.045 (4)	131 (4)
O8—H8···O11 ^{ix}	0.81 (2)	2.01 (4)	2.693 (4)	142 (6)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x, -y + 1, -z$; (iv) $x - 1, y + 1, z$; (v) $x, y + 1, z$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x - 1, y, z$; (x) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (xi) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (xii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

than those of Co^{II} complexes (Mahata *et al.*, 2009) and consistent with the Co^{III} oxidation state (Wahnon *et al.*, 1995; Forster *et al.*, 2005; Zhang *et al.*, 2007; Liu *et al.*, 2015). The Co1···Co2 distance is consistently short [2.7918 (7) Å], with Co—O—Co angles of 92.99 (8) and 93.71 (8)° (O3 and O4, respectively), which is also observed in the Co^{III} complexes of a tetradentate phthalazine ligand (Thompson *et al.*, 2004).

Unlike the coordination modes of the tzCOO²⁻ ligand in complexes (I) and (II), the atzCOO²⁻ ligand in (III) serves as a bidentate ligand in a μ -N¹:N² fashion, in which the carboxylate and amino groups are not involved in coordination with the Co³⁺ ions. As complex (III) was obtained from excess ammonia solutions, the OH⁻ anions may come from the dissociation of ammonia. The NO₃⁻ anion is not coordinated to the Co³⁺ ions and is present only for charge balance, so the complex is an ionic compound. Moreover, an extensive selection of hydrogen bonds exist in the structure (Table 7), described between: (i) ammonia ligands (donors) and uncoordinated nitrate anions (acceptors) or water molecules (acceptors); (ii) ammonia ligands (donors) and carboxylate (acceptors) or amino groups (acceptors) of the atzCOO²⁻

ions; (iii) coordinated hydroxide anions (donors) and carboxylate groups (acceptors) of the atzCOO²⁻ ions; (iv) water (donors) and ammonia ligands (acceptors) or carboxylate groups (acceptors) of the atzCOO²⁻ ions; (v) uncoordinated hydroxide anions (donors) and carboxylate groups of the atzCOO²⁻ ions (acceptors); (vi) crystalline water molecules (donors) and carboxylate groups (acceptors) of the atzCOO²⁻ ions or neighbouring crystalline water molecules (acceptors); (vii) crystalline water molecules (donors) and coordinated hydroxide anions (acceptors) or free nitrate anions (acceptors). These hydrogen bonds lead to the formation of a three-dimensional supramolecular structure (Fig. 7). Hydrogen-bond distances are listed in Table 7. Comparing the three crystal structures, it seems that the coordination modes of the ligands might play an important role in determining the structures. The μ -O,N²:N¹ and μ -O,N⁴:N¹ modes are present in compounds (I) and (II), respectively, while the μ -N¹:N² mode is found in compound (III).

In summary, we have successfully prepared three complexes with 3-amino-1,2,4-triazole-5-carboxylic acid or 1,2,4-triazole-3-carboxylic acid ligands. Uniting the coordination features of triazolate, carboxylate and amino groups, these ligands display versatile coordination modes upon binding to metals, although the amino group is not coordinated in these structures. As the coordination chemistry is very possibly different from that of their symmetric congeners, the present work might also draw attention to the coordination chemistry of asymmetric triazoles, and therefore these findings may be helpful in the construction of metal–organic frameworks with potential practical applications.

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supporting information

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Complexes of nickel(II) and copper(II) with 1,2,4-triazole-3-carboxylic acid and of cobalt(III) with 3-amino-1,2,4-triazole-5-carboxylic acid

Feng-Yi Liu, Dong-Mei Zhou, Xiao-Lan Zhao and Jun-Feng Kou

Computing details

For all structures, data collection: *CrystalStructure* (Rigaku/MSO, 2006); cell refinement: *CrystalStructure*; data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXL2014/7* (Sheldrick, 2015). Program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015) for (I), (III); *SHELXL2014/7* (Sheldrick, 2015)' for (II). For all structures, molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Bis(μ -1,2,4-triazol-4-ide-3-carboxylato)- $\kappa^3N^2,O:N^1;\kappa^3N^1:N^2,O$ -bis[triamminenickel(II)] tetrahydrate (I)

Crystal data

$[\text{Ni}_2(\text{C}_3\text{HN}_3\text{O}_2)_2(\text{NH}_3)_6]\cdot 4\text{H}_2\text{O}$

$M_r = 513.78$

Triclinic, $P\bar{1}$

$a = 7.1226$ (14) Å

$b = 9.0134$ (18) Å

$c = 9.1203$ (18) Å

$\alpha = 103.16$ (3)°

$\beta = 107.48$ (3)°

$\gamma = 106.69$ (3)°

$V = 502.4$ (2) Å³

$Z = 1$

$F(000) = 268$

$D_x = 1.698$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4751 reflections

$\theta = 3.2\text{--}25.0^\circ$

$\mu = 1.94$ mm⁻¹

$T = 293$ K

Block, green

$0.30 \times 0.27 \times 0.25$ mm

Data collection

Rigaku MM007-HF CCD (Saturn 724+) diffractometer

Radiation source: rotating anode

ω scans at fixed $\chi = 45^\circ$

Absorption correction: multi-scan SADABS

$T_{\min} = 0.565$, $T_{\max} = 0.616$

3780 measured reflections

1767 independent reflections

1641 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.071$

$S = 1.06$

1767 reflections

166 parameters

15 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. SHELXTL

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.15773 (4)	0.70968 (3)	0.19786 (3)	0.01892 (12)
N1	0.2355 (3)	0.60104 (19)	0.0094 (2)	0.0205 (4)
N2	0.1393 (3)	0.4702 (2)	-0.1341 (2)	0.0215 (4)
N3	0.0181 (3)	0.8213 (2)	0.0404 (2)	0.0273 (4)
H3A	-0.038 (4)	0.752 (3)	-0.054 (2)	0.033*
H3B	-0.085 (3)	0.844 (3)	0.049 (3)	0.033*
H3C	0.111 (3)	0.907 (2)	0.057 (3)	0.033*
N4	0.4447 (3)	0.6379 (2)	-0.1301 (2)	0.0303 (4)
N5	0.1380 (3)	0.8683 (2)	0.3970 (2)	0.0313 (4)
H5A	0.069 (4)	0.823 (3)	0.454 (3)	0.038*
H5B	0.069 (4)	0.926 (3)	0.368 (3)	0.038*
H5C	0.260 (3)	0.937 (3)	0.471 (3)	0.038*
N6	0.3062 (3)	0.5928 (2)	0.3453 (3)	0.0322 (4)
H6A	0.219 (4)	0.511 (3)	0.356 (3)	0.039*
H6B	0.377 (4)	0.553 (3)	0.299 (3)	0.039*
H6C	0.397 (4)	0.659 (3)	0.442 (2)	0.039*
O1	0.7153 (3)	0.94905 (19)	0.1455 (2)	0.0432 (5)
O2	0.4696 (2)	0.88761 (18)	0.25157 (18)	0.0277 (4)
O3W	0.9480 (3)	0.7541 (2)	0.6383 (2)	0.0469 (5)
H3WA	1.070 (3)	0.820 (3)	0.694 (4)	0.070*
H3WB	0.847 (3)	0.775 (4)	0.652 (4)	0.070*
O4W	0.6083 (3)	0.8219 (2)	0.6953 (2)	0.0375 (4)
H4WA	0.579 (5)	0.769 (3)	0.754 (3)	0.056*
H4WB	0.571 (5)	0.902 (3)	0.700 (4)	0.056*
C1	0.4131 (3)	0.6969 (2)	0.0054 (2)	0.0222 (4)
C2	0.2697 (4)	0.4977 (3)	-0.2127 (3)	0.0294 (5)
H2	0.2422	0.4265	-0.3150	0.035*
C3	0.5471 (3)	0.8585 (3)	0.1445 (3)	0.0262 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01801 (18)	0.01723 (18)	0.01874 (17)	0.00398 (13)	0.00777 (12)	0.00403 (12)
N1	0.0178 (8)	0.0180 (8)	0.0221 (8)	0.0042 (7)	0.0081 (7)	0.0036 (7)
N2	0.0221 (9)	0.0172 (9)	0.0222 (8)	0.0041 (8)	0.0100 (7)	0.0041 (7)

N3	0.0258 (10)	0.0259 (10)	0.0300 (10)	0.0099 (9)	0.0112 (8)	0.0090 (8)
N4	0.0259 (10)	0.0270 (9)	0.0333 (10)	0.0026 (8)	0.0174 (8)	0.0039 (8)
N5	0.0363 (11)	0.0268 (10)	0.0278 (10)	0.0079 (9)	0.0165 (9)	0.0046 (8)
N6	0.0311 (11)	0.0284 (11)	0.0303 (10)	0.0077 (9)	0.0072 (9)	0.0094 (9)
O1	0.0260 (9)	0.0289 (9)	0.0577 (11)	-0.0060 (8)	0.0245 (8)	-0.0050 (8)
O2	0.0229 (8)	0.0233 (7)	0.0293 (8)	0.0036 (7)	0.0110 (6)	0.0014 (6)
O3W	0.0462 (11)	0.0399 (10)	0.0430 (10)	0.0044 (9)	0.0217 (9)	0.0032 (8)
O4W	0.0473 (10)	0.0311 (9)	0.0383 (9)	0.0131 (8)	0.0229 (8)	0.0133 (7)
C1	0.0187 (10)	0.0207 (10)	0.0261 (10)	0.0062 (9)	0.0102 (8)	0.0059 (8)
C2	0.0285 (12)	0.0261 (11)	0.0287 (11)	0.0041 (10)	0.0163 (10)	0.0021 (9)
C3	0.0200 (11)	0.0216 (10)	0.0303 (11)	0.0060 (9)	0.0077 (9)	0.0022 (9)

Geometric parameters (Å, °)

Ni1—N2 ⁱ	2.0745 (19)	N5—H5A	0.904 (17)
Ni1—N1	2.0825 (18)	N5—H5B	0.848 (17)
Ni1—N3	2.106 (2)	N5—H5C	0.863 (17)
Ni1—N5	2.110 (2)	N6—H6A	0.861 (17)
Ni1—N6	2.114 (2)	N6—H6B	0.857 (17)
Ni1—O2	2.1651 (18)	N6—H6C	0.864 (17)
N1—C1	1.327 (3)	O1—C3	1.237 (3)
N1—N2	1.367 (2)	O2—C3	1.272 (3)
N2—C2	1.337 (3)	O3W—H3WA	0.814 (17)
N2—Ni1 ⁱ	2.0745 (19)	O3W—H3WB	0.835 (17)
N3—H3A	0.831 (16)	O4W—H4WA	0.827 (17)
N3—H3B	0.833 (17)	O4W—H4WB	0.833 (17)
N3—H3C	0.805 (16)	C1—C3	1.508 (3)
N4—C1	1.341 (3)	C2—H2	0.9300
N4—C2	1.348 (3)		
N2 ⁱ —Ni1—N1	99.08 (7)	H3B—N3—H3C	107 (3)
N2 ⁱ —Ni1—N3	90.35 (8)	C1—N4—C2	101.33 (18)
N1—Ni1—N3	86.20 (8)	Ni1—N5—H5A	118.3 (16)
N2 ⁱ —Ni1—N5	93.72 (9)	Ni1—N5—H5B	112.4 (18)
N1—Ni1—N5	166.82 (7)	H5A—N5—H5B	101 (2)
N3—Ni1—N5	90.62 (8)	Ni1—N5—H5C	113.6 (17)
N2 ⁱ —Ni1—N6	90.82 (8)	H5A—N5—H5C	104 (2)
N1—Ni1—N6	90.24 (8)	H5B—N5—H5C	106 (2)
N3—Ni1—N6	176.38 (8)	Ni1—N6—H6A	114.2 (19)
N5—Ni1—N6	92.72 (9)	Ni1—N6—H6B	107.5 (19)
N2 ⁱ —Ni1—O2	176.40 (6)	H6A—N6—H6B	106 (2)
N1—Ni1—O2	77.32 (7)	Ni1—N6—H6C	113.8 (18)
N3—Ni1—O2	89.58 (8)	H6A—N6—H6C	108 (3)
N5—Ni1—O2	89.88 (8)	H6B—N6—H6C	106 (2)
N6—Ni1—O2	89.05 (8)	C3—O2—Ni1	115.74 (12)
C1—N1—N2	106.05 (17)	H3WA—O3W—H3WB	120 (3)
C1—N1—Ni1	114.02 (13)	H4WA—O4W—H4WB	116 (3)
N2—N1—Ni1	138.46 (13)	N1—C1—N4	113.83 (17)

C2—N2—N1	104.97 (16)	N1—C1—C3	118.14 (18)
C2—N2—Ni1 ⁱ	133.02 (14)	N4—C1—C3	127.96 (19)
N1—N2—Ni1 ⁱ	121.86 (14)	N2—C2—N4	113.81 (18)
Ni1—N3—H3A	106.7 (17)	N2—C2—H2	123.1
Ni1—N3—H3B	118.6 (19)	N4—C2—H2	123.1
H3A—N3—H3B	101 (3)	O1—C3—O2	126.26 (18)
Ni1—N3—H3C	106.5 (19)	O1—C3—C1	119.6 (2)
H3A—N3—H3C	117 (3)	O2—C3—C1	114.12 (18)

Symmetry code: (i) $-x, -y+1, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3B \cdots O1 ⁱⁱ	0.83 (2)	2.20 (2)	3.010 (3)	163 (2)
N3—H3C \cdots O4W ⁱⁱⁱ	0.81 (2)	2.65 (2)	3.307 (3)	139 (2)
N5—H5A \cdots O3W ⁱⁱ	0.90 (2)	2.23 (2)	3.123 (3)	168 (2)
N5—H5C \cdots O2 ⁱⁱⁱ	0.86 (2)	2.47 (2)	3.286 (3)	157 (2)
N6—H6A \cdots O3W ^{iv}	0.86 (2)	2.37 (2)	3.193 (3)	161 (3)
N6—H6C \cdots O4W	0.86 (2)	2.21 (2)	3.067 (3)	175 (3)
O3W—H3WA \cdots O1 ^v	0.81 (2)	2.07 (2)	2.805 (3)	151 (3)
O3W—H3WB \cdots O4W	0.84 (2)	1.99 (2)	2.821 (3)	177 (4)
O4W—H4WA \cdots N4 ^{vi}	0.83 (2)	1.99 (2)	2.802 (3)	168 (3)
O4W—H4WB \cdots O2 ⁱⁱⁱ	0.83 (2)	1.97 (2)	2.795 (2)	169 (3)

Symmetry codes: (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+2, -y+2, -z+1$; (vi) $x, y, z+1$.

catena-Poly[[[diamminediaquacopper(II)]- μ -1,2,4-triazol-4-ide-3-carboxylato- $\kappa^3 N^1:N^4, O$ -[diamminecopper(II)]- μ -1,2,4-triazol-4-ide-3-carboxylato- $\kappa^3 N^4, O:N^1$] dihydrate] (II)

Crystal data

$[\text{Cu}(\text{C}_3\text{HN}_3\text{O}_2)(\text{NH}_3)_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$

$M_r = 244.72$

Triclinic, $P\bar{1}$

$a = 7.2183$ (14) \AA

$b = 7.4079$ (15) \AA

$c = 9.887$ (2) \AA

$\alpha = 72.45$ (3) $^\circ$

$\beta = 68.82$ (3) $^\circ$

$\gamma = 62.74$ (3) $^\circ$

$V = 432.3$ (2) \AA^3

$Z = 2$

$F(000) = 250$

$D_x = 1.880$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 4227 reflections

$\theta = 3.1\text{--}25.0^\circ$

$\mu = 2.52$ mm^{-1}

$T = 293$ K

Block, blue

$0.31 \times 0.28 \times 0.26$ mm

Data collection

Rigaku MM007-HF CCD (Saturn 724+) diffractometer

Radiation source: rotating anode

ω scans at fixed $\chi = 45^\circ$

Absorption correction: multi-scan

SADABS

$T_{\min} = 0.509$, $T_{\max} = 0.560$

3353 measured reflections

1500 independent reflections

1248 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -8 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.145$

$S = 1.04$

1500 reflections

123 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.094P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.40 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. SHELXTL

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.0203 (3)
Cu2	1.0000	0.0000	0.0000	0.0256 (3)
N1	0.8601 (6)	0.0948 (5)	0.1951 (4)	0.0275 (8)
N2	0.8583 (6)	-0.0372 (5)	0.3266 (4)	0.0262 (8)
N3	1.1397 (6)	0.2126 (6)	-0.0815 (4)	0.0377 (9)
H3A	1.0438	0.3343	-0.1110	0.056*
H3B	1.2534	0.1717	-0.1574	0.056*
H3C	1.1822	0.2236	-0.0114	0.056*
N4	0.6732 (5)	0.2867 (5)	0.3698 (4)	0.0210 (7)
N5	0.7753 (5)	0.5002 (6)	0.5067 (5)	0.0391 (10)
H5A	0.7865	0.4597	0.5988	0.059*
H5B	0.7736	0.6268	0.4744	0.059*
H5C	0.8877	0.4143	0.4498	0.059*
O1	0.7837 (6)	-0.1767 (5)	0.6347 (4)	0.0396 (9)
O2	0.5882 (5)	0.1518 (5)	0.6707 (3)	0.0312 (7)
O3W	1.3282 (5)	-0.2432 (5)	0.1031 (4)	0.0441 (9)
H3WA	1.4356	-0.2944	0.0389	0.066*
H3WB	1.3217	-0.1799	0.1630	0.066*
O4W	0.2790 (7)	0.3937 (6)	0.1034 (4)	0.0468 (10)
H4WA	0.3110	0.2747	0.1495	0.070*
H4WB	0.2756	0.4872	0.1344	0.070*
C1	0.7449 (6)	0.0841 (6)	0.4283 (4)	0.0221 (9)
C2	0.7486 (6)	0.2854 (7)	0.2241 (5)	0.0272 (10)
H2	0.7255	0.4030	0.1528	0.033*
C3	0.7024 (7)	0.0138 (7)	0.5917 (5)	0.0257 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0205 (4)	0.0178 (4)	0.0216 (5)	-0.0045 (3)	-0.0007 (3)	-0.0129 (3)
Cu2	0.0368 (5)	0.0207 (5)	0.0150 (4)	-0.0105 (3)	0.0022 (3)	-0.0097 (3)
N1	0.0379 (19)	0.0169 (17)	0.0193 (18)	-0.0053 (15)	-0.0025 (16)	-0.0069 (14)
N2	0.0356 (19)	0.0199 (17)	0.0173 (17)	-0.0071 (14)	-0.0006 (15)	-0.0090 (14)
N3	0.042 (2)	0.040 (2)	0.034 (2)	-0.0165 (18)	-0.0026 (18)	-0.0167 (18)
N4	0.0249 (16)	0.0171 (16)	0.0167 (16)	-0.0040 (14)	-0.0012 (14)	-0.0094 (14)
N5	0.0250 (18)	0.035 (2)	0.063 (3)	-0.0070 (16)	-0.0108 (18)	-0.025 (2)
O1	0.061 (2)	0.0268 (18)	0.0216 (17)	-0.0126 (16)	-0.0044 (16)	-0.0059 (15)
O2	0.0408 (16)	0.0273 (16)	0.0186 (14)	-0.0091 (13)	0.0001 (13)	-0.0113 (13)
O3W	0.051 (2)	0.044 (2)	0.0364 (19)	-0.0145 (16)	-0.0108 (16)	-0.0119 (17)
O4W	0.066 (2)	0.041 (2)	0.031 (2)	-0.0219 (19)	-0.0108 (19)	-0.0029 (17)
C1	0.029 (2)	0.0179 (19)	0.017 (2)	-0.0095 (16)	-0.0018 (17)	-0.0053 (16)
C2	0.036 (2)	0.022 (2)	0.020 (2)	-0.0079 (18)	-0.0001 (19)	-0.0125 (17)
C3	0.030 (2)	0.026 (2)	0.022 (2)	-0.0106 (18)	-0.0021 (18)	-0.0100 (19)

Geometric parameters (\AA , $^\circ$)

Cu1—N4 ⁱ	1.992 (3)	N3—H3B	0.8900
Cu1—N4	1.992 (3)	N3—H3C	0.8900
Cu1—N5	2.013 (3)	N4—C2	1.345 (5)
Cu1—N5 ⁱ	2.013 (3)	N4—C1	1.355 (5)
Cu1—O2 ⁱ	2.560 (3)	N5—H5A	0.8900
Cu1—O2	2.560 (3)	N5—H5B	0.8900
Cu2—N1	1.999 (3)	N5—H5C	0.8900
Cu2—N1 ⁱⁱ	1.999 (3)	O1—C3	1.256 (6)
Cu2—N3	2.061 (4)	O2—C3	1.256 (5)
Cu2—N3 ⁱⁱ	2.061 (4)	O3W—H3WA	0.8171
Cu2—O3W	2.574 (3)	O3W—H3WB	0.8365
Cu2—O3W ⁱⁱ	2.574 (3)	O4W—H4WA	0.8282
N1—C2	1.327 (5)	O4W—H4WB	0.8248
N1—N2	1.370 (5)	C1—C3	1.502 (6)
N2—C1	1.329 (5)	C2—H2	0.9300
N3—H3A	0.8900		
N4 ⁱ —Cu1—N4	180.00 (16)	N2—N1—Cu2	123.3 (3)
N4 ⁱ —Cu1—N5	90.48 (14)	C1—N2—N1	104.9 (3)
N4—Cu1—N5	89.52 (14)	Cu2—N3—H3A	109.5
N4 ⁱ —Cu1—N5 ⁱ	89.52 (14)	Cu2—N3—H3B	109.5
N4—Cu1—N5 ⁱ	90.48 (14)	H3A—N3—H3B	109.5
N5—Cu1—N5 ⁱ	180.0	Cu2—N3—H3C	109.5
N4 ⁱ —Cu1—O2 ⁱ	73.78 (12)	H3A—N3—H3C	109.5
N4—Cu1—O2 ⁱ	106.22 (12)	H3B—N3—H3C	109.5
N5—Cu1—O2 ⁱ	92.24 (14)	C2—N4—C1	103.3 (3)
N5 ⁱ —Cu1—O2 ⁱ	87.76 (14)	C2—N4—Cu1	136.3 (3)
N4 ⁱ —Cu1—O2	106.22 (12)	C1—N4—Cu1	120.4 (3)

N4—Cu1—O2	73.78 (12)	Cu1—N5—H5A	109.5
N5—Cu1—O2	87.76 (14)	Cu1—N5—H5B	109.5
N5 ⁱ —Cu1—O2	92.24 (14)	H5A—N5—H5B	109.5
O2 ⁱ —Cu1—O2	180.0	Cu1—N5—H5C	109.5
N1—Cu2—N1 ⁱⁱ	180.0	H5A—N5—H5C	109.5
N1—Cu2—N3	91.79 (15)	H5B—N5—H5C	109.5
N1 ⁱⁱ —Cu2—N3	88.21 (15)	C3—O2—Cu1	107.8 (2)
N1—Cu2—N3 ⁱⁱ	88.21 (15)	Cu2—O3W—H3WA	112.1
N1 ⁱⁱ —Cu2—N3 ⁱⁱ	91.79 (15)	Cu2—O3W—H3WB	103.6
N3—Cu2—N3 ⁱⁱ	180.0	H3WA—O3W—H3WB	125.4
N1—Cu2—O3W	86.07 (13)	H4WA—O4W—H4WB	121.7
N1 ⁱⁱ —Cu2—O3W	93.93 (13)	N2—C1—N4	112.7 (3)
N3—Cu2—O3W	87.72 (13)	N2—C1—C3	125.8 (3)
N3 ⁱⁱ —Cu2—O3W	92.28 (13)	N4—C1—C3	121.4 (3)
N1—Cu2—O3W ⁱⁱ	93.93 (13)	N1—C2—N4	111.3 (4)
N1 ⁱⁱ —Cu2—O3W ⁱⁱ	86.07 (13)	N1—C2—H2	124.4
N3—Cu2—O3W ⁱⁱ	92.28 (13)	N4—C2—H2	124.4
N3 ⁱⁱ —Cu2—O3W ⁱⁱ	87.72 (13)	O1—C3—O2	127.0 (4)
O3W—Cu2—O3W ⁱⁱ	180.0	O1—C3—C1	116.5 (4)
C2—N1—N2	107.8 (3)	O2—C3—C1	116.5 (4)
C2—N1—Cu2	128.8 (3)		
C2—N1—N2—C1	-0.4 (4)	Cu2—N1—C2—N4	177.8 (3)
Cu2—N1—N2—C1	-177.9 (3)	C1—N4—C2—N1	-0.4 (4)
N1—N2—C1—N4	0.1 (4)	Cu1—N4—C2—N1	179.5 (3)
N1—N2—C1—C3	-177.7 (4)	Cu1—O2—C3—O1	177.6 (4)
C2—N4—C1—N2	0.1 (4)	Cu1—O2—C3—C1	-2.9 (4)
Cu1—N4—C1—N2	-179.8 (3)	N2—C1—C3—O1	0.7 (6)
C2—N4—C1—C3	178.1 (4)	N4—C1—C3—O1	-177.0 (4)
Cu1—N4—C1—C3	-1.8 (5)	N2—C1—C3—O2	-178.9 (4)
N2—N1—C2—N4	0.5 (5)	N4—C1—C3—O2	3.5 (6)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A \cdots O4W ⁱⁱⁱ	0.89	2.27	3.115 (6)	158
N3—H3B \cdots O2 ^{iv}	0.89	2.37	3.207 (5)	157
N3—H3C \cdots O4W ^v	0.89	2.37	3.194 (5)	154
N5—H5B \cdots O1 ^{vi}	0.89	2.49	3.057 (5)	122
N5—H5C \cdots O1 ^{vii}	0.89	2.25	3.106 (5)	162
O3W—H3WA \cdots O4W ⁱⁱ	0.82	1.98	2.783 (6)	169
O3W—H3WB \cdots O2 ^{vii}	0.84	2.07	2.844 (4)	154
O4W—H4WA \cdots O1 ^{viii}	0.83	2.00	2.608 (5)	129

O4W—H4WB···O3W ^{ix}	0.82	2.11	2.869 (5)	152
C2—H2···O4W ⁱⁱⁱ	0.93	2.53	3.401 (7)	156

Symmetry codes: (ii) $-x+2, -y, -z$; (iii) $-x+1, -y+1, -z$; (iv) $x+1, y, z-1$; (v) $x+1, y, z$; (vi) $x, y+1, z$; (vii) $-x+2, -y, -z+1$; (viii) $-x+1, -y, -z+1$; (ix) $x-1, y+1, z$.

(μ -5-Amino-1,2,4-triazol-1-ide-3-carboxylato- $\kappa^2N^1:N^2$)di- μ -hydroxido- κ^4O :O-bis[triammincobalt(III)] nitrate hydroxide trihydrate (III)

Crystal data

[Co₂(C₃H₂N₄O₂)(OH)₂(NH₃)₆](NO₃)(OH)·3H₂O
M_r = 513.23
 Monoclinic, *P*2₁/*n*
a = 7.0765 (14) Å
b = 12.676 (3) Å
c = 20.591 (4) Å
 β = 98.70 (3)°
V = 1825.8 (6) Å³
Z = 4

F(000) = 1064
D_x = 1.867 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 17515 reflections
 θ = 3.2–25.0°
 μ = 1.89 mm⁻¹
T = 293 K
 Block, red
 0.31 × 0.28 × 0.26 mm

Data collection

Rigaku MM007-HF CCD (Saturn 724+) diffractometer
 Radiation source: rotating anode
 ω scans at fixed χ = 45°
 Absorption correction: multi-scan SADABS
T_{min} = 0.561, *T_{max}* = 0.611
 13577 measured reflections

3212 independent reflections
 2940 reflections with *I* > 2 σ (*I*)
R_{int} = 0.043
 θ_{\max} = 25.0°, θ_{\min} = 3.2°
h = -8→8
k = -15→15
l = -24→24

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2 σ (*F*²)] = 0.031
wR(*F*²) = 0.084
S = 1.06
 3212 reflections
 332 parameters
 31 restraints
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 Only H-atom coordinates refined
 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 1.1006P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.50 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. SHELXTL

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Co1	0.33049 (4)	0.79322 (2)	0.06762 (2)	0.02144 (12)
Co2	0.33651 (4)	0.60722 (3)	0.14051 (2)	0.02182 (12)

N1	0.2789 (3)	0.67233 (16)	0.01205 (10)	0.0232 (4)
N2	0.2814 (3)	0.57823 (16)	0.04587 (10)	0.0226 (4)
N3	0.2088 (4)	0.7206 (2)	-0.10064 (12)	0.0387 (6)
H3A	0.188 (5)	0.695 (3)	-0.1392 (11)	0.046*
H3B	0.227 (5)	0.7861 (16)	-0.0923 (17)	0.046*
N4	0.2058 (3)	0.54445 (17)	-0.06113 (10)	0.0270 (5)
N5	0.1132 (4)	0.87067 (19)	0.02078 (12)	0.0318 (5)
H5A	0.149 (5)	0.907 (2)	-0.0110 (13)	0.038*
H5B	0.016 (4)	0.828 (2)	0.0091 (16)	0.038*
H5C	0.068 (4)	0.913 (2)	0.0483 (14)	0.038*
N6	0.5164 (3)	0.84978 (19)	0.01593 (11)	0.0294 (5)
H6A	0.459 (4)	0.875 (2)	-0.0207 (11)	0.035*
H6B	0.587 (4)	0.800 (2)	0.0073 (16)	0.035*
H6C	0.591 (4)	0.897 (2)	0.0371 (15)	0.035*
N7	0.3866 (4)	0.90708 (19)	0.13095 (12)	0.0308 (5)
H7A	0.291 (3)	0.943 (2)	0.1391 (15)	0.037*
H7B	0.471 (4)	0.953 (2)	0.1272 (16)	0.037*
H7C	0.443 (4)	0.887 (2)	0.1675 (11)	0.037*
N8	0.3956 (3)	0.6511 (2)	0.23194 (11)	0.0302 (5)
H8A	0.302 (3)	0.678 (2)	0.2467 (15)	0.036*
H8B	0.476 (4)	0.7030 (19)	0.2360 (16)	0.036*
H8C	0.448 (4)	0.604 (2)	0.2595 (14)	0.036*
N9	0.5203 (3)	0.4948 (2)	0.15522 (12)	0.0308 (5)
H9A	0.611 (4)	0.508 (2)	0.1343 (14)	0.037*
H9B	0.570 (4)	0.485 (2)	0.1949 (10)	0.037*
H9C	0.471 (4)	0.4377 (18)	0.1417 (15)	0.037*
N10	0.1319 (3)	0.51865 (19)	0.16301 (11)	0.0298 (5)
H10A	0.076 (4)	0.549 (2)	0.1921 (13)	0.036*
H10B	0.163 (4)	0.4578 (17)	0.1761 (15)	0.036*
H10C	0.052 (4)	0.504 (2)	0.1293 (12)	0.036*
N11	0.8447 (4)	0.0130 (2)	0.13634 (13)	0.0446 (6)
O1	0.2654 (4)	0.35777 (16)	0.07150 (10)	0.0466 (5)
O2	0.1859 (3)	0.32897 (15)	-0.03610 (10)	0.0376 (5)
O3	0.1700 (2)	0.72718 (14)	0.12350 (9)	0.0249 (4)
H3	0.075 (3)	0.706 (2)	0.1033 (15)	0.037*
O4	0.5190 (2)	0.70912 (14)	0.12014 (9)	0.0251 (4)
H4	0.596 (5)	0.688 (3)	0.0980 (17)	0.038*
O9	0.7091 (3)	0.03208 (18)	0.09060 (10)	0.0467 (5)
O10	0.8116 (4)	-0.00371 (19)	0.19519 (10)	0.0519 (6)
O11	1.0152 (3)	0.0116 (2)	0.12508 (16)	0.0673 (8)
O5W	0.2034 (4)	0.6831 (2)	0.75766 (12)	0.0513 (6)
H5WA	0.294 (5)	0.727 (3)	0.755 (2)	0.077*
H5WB	0.216 (6)	0.625 (2)	0.738 (2)	0.077*
O6W	0.9492 (4)	0.6341 (2)	0.26977 (13)	0.0634 (7)
H6WA	1.028 (6)	0.656 (4)	0.3010 (18)	0.095*
H6WB	0.867 (5)	0.591 (3)	0.277 (2)	0.095*
O7W	0.3576 (4)	0.3604 (2)	0.26183 (13)	0.0573 (6)
H7WA	0.378 (6)	0.311 (2)	0.2906 (18)	0.086*

H7WB	0.433 (6)	0.415 (2)	0.274 (2)	0.089 (16)*
O8	0.2846 (4)	0.1600 (2)	0.11963 (18)	0.0751 (9)
H8	0.176 (4)	0.141 (4)	0.118 (3)	0.113*
C1	0.2316 (4)	0.6490 (2)	-0.05156 (12)	0.0251 (5)
C2	0.2390 (3)	0.5042 (2)	0.00024 (12)	0.0241 (5)
C3	0.2281 (4)	0.3871 (2)	0.01313 (14)	0.0286 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02478 (19)	0.0212 (2)	0.01836 (19)	0.00119 (13)	0.00348 (13)	-0.00048 (12)
Co2	0.02290 (19)	0.0251 (2)	0.01751 (19)	0.00129 (13)	0.00339 (13)	0.00115 (12)
N1	0.0297 (11)	0.0215 (10)	0.0184 (10)	0.0016 (8)	0.0038 (8)	0.0013 (8)
N2	0.0260 (10)	0.0212 (10)	0.0212 (10)	0.0026 (8)	0.0052 (8)	0.0018 (8)
N3	0.0650 (17)	0.0313 (13)	0.0187 (12)	-0.0036 (12)	0.0024 (11)	0.0007 (10)
N4	0.0321 (11)	0.0279 (11)	0.0211 (11)	-0.0001 (9)	0.0044 (8)	-0.0037 (9)
N5	0.0364 (13)	0.0314 (13)	0.0272 (12)	0.0081 (10)	0.0034 (10)	0.0037 (10)
N6	0.0356 (12)	0.0267 (12)	0.0273 (12)	0.0008 (10)	0.0094 (10)	0.0029 (9)
N7	0.0330 (12)	0.0291 (12)	0.0301 (12)	-0.0025 (10)	0.0037 (10)	-0.0067 (10)
N8	0.0324 (12)	0.0376 (13)	0.0205 (11)	-0.0004 (10)	0.0035 (9)	0.0014 (10)
N9	0.0323 (12)	0.0338 (13)	0.0271 (12)	0.0061 (10)	0.0066 (10)	0.0057 (10)
N10	0.0315 (12)	0.0315 (12)	0.0268 (12)	-0.0039 (10)	0.0058 (9)	-0.0004 (10)
N11	0.0459 (15)	0.0354 (14)	0.0518 (17)	-0.0039 (11)	0.0048 (13)	-0.0054 (12)
O1	0.0716 (15)	0.0281 (11)	0.0386 (12)	-0.0008 (11)	0.0038 (11)	0.0066 (9)
O2	0.0411 (11)	0.0277 (10)	0.0435 (12)	-0.0003 (8)	0.0050 (9)	-0.0099 (9)
O3	0.0232 (8)	0.0288 (9)	0.0232 (9)	0.0009 (7)	0.0048 (7)	-0.0013 (7)
O4	0.0237 (9)	0.0299 (10)	0.0219 (9)	-0.0004 (7)	0.0038 (7)	0.0015 (7)
O9	0.0481 (12)	0.0513 (13)	0.0352 (11)	-0.0065 (10)	-0.0109 (10)	0.0101 (10)
O10	0.0730 (16)	0.0571 (14)	0.0247 (11)	-0.0018 (12)	0.0050 (10)	0.0097 (10)
O11	0.0359 (13)	0.0616 (16)	0.109 (2)	0.0006 (11)	0.0262 (13)	-0.0167 (15)
O5W	0.0575 (15)	0.0589 (15)	0.0378 (13)	0.0175 (12)	0.0080 (11)	0.0011 (11)
O6W	0.0737 (19)	0.0684 (18)	0.0539 (16)	-0.0044 (14)	0.0288 (13)	0.0037 (14)
O7W	0.0602 (15)	0.0557 (16)	0.0575 (16)	-0.0088 (13)	0.0134 (12)	0.0070 (13)
O8	0.0528 (15)	0.0547 (17)	0.118 (3)	0.0005 (13)	0.0132 (17)	0.0362 (17)
C1	0.0283 (12)	0.0277 (13)	0.0192 (12)	0.0026 (10)	0.0033 (10)	-0.0011 (10)
C2	0.0210 (11)	0.0261 (13)	0.0258 (12)	0.0011 (10)	0.0053 (9)	-0.0018 (10)
C3	0.0257 (13)	0.0227 (13)	0.0386 (16)	0.0013 (10)	0.0088 (11)	-0.0024 (11)

Geometric parameters (Å, °)

Co1—O4	1.9103 (18)	N7—H7B	0.844 (18)
Co1—N1	1.914 (2)	N7—H7C	0.838 (18)
Co1—O3	1.9261 (19)	N8—H8A	0.842 (18)
Co1—N7	1.945 (2)	N8—H8B	0.867 (18)
Co1—N6	1.950 (2)	N8—H8C	0.870 (18)
Co1—N5	1.952 (2)	N9—H9A	0.844 (18)
Co2—O4	1.9174 (18)	N9—H9B	0.849 (18)
Co2—N9	1.922 (2)	N9—H9C	0.833 (18)

Co2—O3	1.9231 (18)	N10—H10A	0.858 (18)
Co2—N10	1.943 (2)	N10—H10B	0.835 (18)
Co2—N8	1.947 (2)	N10—H10C	0.847 (18)
Co2—N2	1.963 (2)	N11—O9	1.262 (3)
N1—C1	1.335 (3)	N11—O11	1.263 (3)
N1—N2	1.380 (3)	N11—O10	1.286 (3)
N2—C2	1.330 (3)	O1—C3	1.248 (4)
N3—C1	1.350 (4)	O2—C3	1.252 (3)
N3—H3A	0.848 (18)	O3—H3	0.783 (18)
N3—H3B	0.855 (18)	O4—H4	0.81 (4)
N4—C1	1.348 (3)	O5W—H5WA	0.859 (19)
N4—C2	1.350 (3)	O5W—H5WB	0.849 (19)
N5—H5A	0.869 (18)	O6W—H6WA	0.830 (19)
N5—H5B	0.880 (18)	O6W—H6WB	0.833 (19)
N5—H5C	0.878 (18)	O7W—H7WA	0.859 (18)
N6—H6A	0.863 (18)	O7W—H7WB	0.885 (19)
N6—H6B	0.845 (18)	O8—H8	0.81 (2)
N6—H6C	0.875 (18)	C2—C3	1.512 (3)
N7—H7A	0.848 (18)		
O4—Co1—N1	86.87 (8)	Co1—N6—H6C	113 (2)
O4—Co1—O3	81.01 (8)	H6A—N6—H6C	110 (3)
N1—Co1—O3	86.14 (8)	H6B—N6—H6C	107 (3)
O4—Co1—N7	88.87 (9)	Co1—N7—H7A	116 (2)
N1—Co1—N7	174.69 (10)	Co1—N7—H7B	122 (2)
O3—Co1—N7	90.06 (10)	H7A—N7—H7B	104 (3)
O4—Co1—N6	92.47 (9)	Co1—N7—H7C	113 (2)
N1—Co1—N6	92.95 (10)	H7A—N7—H7C	106 (3)
O3—Co1—N6	173.46 (9)	H7B—N7—H7C	93 (3)
N7—Co1—N6	90.41 (11)	Co2—N8—H8A	114 (2)
O4—Co1—N5	172.28 (10)	Co2—N8—H8B	111 (2)
N1—Co1—N5	92.43 (10)	H8A—N8—H8B	101 (3)
O3—Co1—N5	91.27 (10)	Co2—N8—H8C	116 (2)
N7—Co1—N5	91.36 (11)	H8A—N8—H8C	109 (3)
N6—Co1—N5	95.24 (11)	H8B—N8—H8C	105 (3)
O4—Co2—N9	94.12 (10)	Co2—N9—H9A	109 (2)
O4—Co2—O3	80.90 (8)	Co2—N9—H9B	116 (2)
N9—Co2—O3	175.01 (9)	H9A—N9—H9B	106 (3)
O4—Co2—N10	172.94 (9)	Co2—N9—H9C	111 (2)
N9—Co2—N10	92.57 (11)	H9A—N9—H9C	109 (3)
O3—Co2—N10	92.41 (9)	H9B—N9—H9C	107 (3)
O4—Co2—N8	88.05 (9)	Co2—N10—H10A	111 (2)
N9—Co2—N8	91.04 (11)	Co2—N10—H10B	116 (2)
O3—Co2—N8	89.22 (9)	H10A—N10—H10B	108 (3)
N10—Co2—N8	89.60 (10)	Co2—N10—H10C	111 (2)
O4—Co2—N2	87.02 (8)	H10A—N10—H10C	111 (3)
N9—Co2—N2	92.61 (10)	H10B—N10—H10C	99 (3)
O3—Co2—N2	86.73 (8)	O9—N11—O11	120.4 (3)

N10—Co2—N2	94.90 (9)	O9—N11—O10	120.6 (3)
N8—Co2—N2	174.07 (10)	O11—N11—O10	119.1 (3)
C1—N1—N2	106.60 (19)	Co2—O3—Co1	92.99 (8)
C1—N1—Co1	139.54 (18)	Co2—O3—H3	106 (2)
N2—N1—Co1	113.79 (15)	Co1—O3—H3	112 (3)
C2—N2—N1	105.60 (19)	Co1—O4—Co2	93.66 (8)
C2—N2—Co2	145.40 (18)	Co1—O4—H4	110 (2)
N1—N2—Co2	108.95 (14)	Co2—O4—H4	116 (2)
C1—N3—H3A	116 (2)	H5WA—O5W—H5WB	113 (3)
C1—N3—H3B	120 (2)	H6WA—O6W—H6WB	118 (3)
H3A—N3—H3B	124 (3)	H7WA—O7W—H7WB	110 (3)
C1—N4—C2	103.5 (2)	N1—C1—N4	111.7 (2)
Co1—N5—H5A	110 (2)	N1—C1—N3	124.7 (2)
Co1—N5—H5B	110 (2)	N4—C1—N3	123.6 (2)
H5A—N5—H5B	115 (3)	N2—C2—N4	112.6 (2)
Co1—N5—H5C	109 (2)	N2—C2—C3	125.5 (2)
H5A—N5—H5C	110 (3)	N4—C2—C3	121.9 (2)
H5B—N5—H5C	102 (3)	O1—C3—O2	126.5 (2)
Co1—N6—H6A	110 (2)	O1—C3—C2	116.9 (2)
Co1—N6—H6B	108 (2)	O2—C3—C2	116.6 (2)
H6A—N6—H6B	108 (3)		
C1—N1—N2—C2	1.1 (3)	N1—N2—C2—N4	-1.1 (3)
Co1—N1—N2—C2	178.61 (15)	Co2—N2—C2—N4	175.8 (2)
C1—N1—N2—Co2	-176.96 (16)	N1—N2—C2—C3	178.7 (2)
Co1—N1—N2—Co2	0.51 (19)	Co2—N2—C2—C3	-4.4 (5)
N2—N1—C1—N4	-0.9 (3)	C1—N4—C2—N2	0.5 (3)
Co1—N1—C1—N4	-177.30 (19)	C1—N4—C2—C3	-179.3 (2)
N2—N1—C1—N3	178.1 (3)	N2—C2—C3—O1	-1.3 (4)
Co1—N1—C1—N3	1.6 (4)	N4—C2—C3—O1	178.5 (2)
C2—N4—C1—N1	0.2 (3)	N2—C2—C3—O2	180.0 (2)
C2—N4—C1—N3	-178.7 (3)	N4—C2—C3—O2	-0.2 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3A...O5W ⁱ	0.85 (2)	2.15 (2)	2.951 (3)	158 (3)
N3—H3B...O9 ⁱⁱ	0.86 (2)	2.35 (2)	3.190 (3)	169 (3)
N5—H5A...O9 ⁱⁱ	0.87 (2)	2.19 (2)	3.039 (3)	166 (3)
N5—H5B...O2 ⁱⁱⁱ	0.88 (2)	2.56 (2)	3.344 (3)	149 (3)
N5—H5C...O11 ^{iv}	0.88 (2)	2.09 (2)	2.955 (4)	168 (3)
N6—H6A...O9 ⁱⁱ	0.86 (2)	2.09 (2)	2.922 (3)	163 (3)
N6—H6B...O2 ⁱⁱ	0.85 (2)	2.30 (2)	3.079 (3)	153 (3)
N6—H6C...O9 ^v	0.88 (2)	2.13 (2)	2.988 (3)	166 (3)
N7—H7A...O11 ^{iv}	0.85 (2)	2.12 (2)	2.929 (3)	159 (3)
N7—H7A...O7W ^{vi}	0.85 (2)	2.65 (3)	3.060 (4)	111 (3)
N7—H7B...O9 ^v	0.84 (2)	2.19 (2)	2.997 (3)	160 (3)
N7—H7B...O10 ^v	0.84 (2)	2.66 (3)	3.297 (4)	134 (3)

N7—H7C...O5W ^{vii}	0.84 (2)	2.57 (2)	3.372 (4)	161 (3)
N8—H8A...O7W ^{vi}	0.84 (2)	2.56 (3)	3.215 (4)	135 (3)
N8—H8B...O5W ^{vii}	0.87 (2)	2.16 (2)	3.016 (3)	171 (3)
N8—H8C...N11 ^{viii}	0.87 (2)	2.67 (2)	3.506 (4)	162 (3)
N8—H8C...O10 ^{viii}	0.87 (2)	2.27 (2)	3.075 (3)	154 (3)
N8—H8C...O11 ^{viii}	0.87 (2)	2.62 (2)	3.411 (4)	151 (3)
N9—H9A...N4 ⁱⁱ	0.84 (2)	2.23 (2)	2.982 (3)	148 (3)
N9—H9B...O10 ^{viii}	0.85 (2)	2.30 (2)	3.130 (3)	167 (3)
N9—H9C...O1	0.83 (2)	2.14 (2)	2.881 (3)	148 (3)
N10—H10A...O6W ^{ix}	0.86 (2)	2.23 (2)	3.083 (4)	176 (3)
N10—H10B...O7W	0.84 (2)	2.41 (2)	3.120 (4)	143 (3)
N10—H10C...N4 ⁱⁱⁱ	0.85 (2)	2.21 (2)	3.039 (3)	165 (3)
O3—H3...O2 ⁱⁱⁱ	0.78 (2)	2.18 (2)	2.952 (3)	170 (3)
O4—H4...O2 ⁱⁱ	0.81 (4)	2.15 (4)	2.947 (3)	166 (3)
O5W—H5WA...O6W ^x	0.86 (2)	2.07 (2)	2.886 (4)	157 (4)
O5W—H5WB...O10 ^{xi}	0.85 (2)	1.95 (2)	2.776 (3)	165 (4)
O6W—H6WA...O8 ^{viii}	0.83 (2)	1.94 (3)	2.746 (4)	162 (5)
O6W—H6WB...N11 ^{viii}	0.83 (2)	2.68 (3)	3.411 (4)	148 (4)
O6W—H6WB...O10 ^{viii}	0.83 (2)	1.89 (2)	2.717 (4)	174 (5)
O7W—H7WA...O3 ^{xii}	0.86 (2)	2.13 (3)	2.933 (3)	155 (5)
O7W—H7WB...N11 ^{viii}	0.89 (2)	2.56 (3)	3.353 (4)	149 (4)
O7W—H7WB...O10 ^{viii}	0.89 (2)	2.10 (3)	2.933 (4)	158 (4)
O7W—H7WB...O11 ^{viii}	0.89 (2)	2.39 (4)	3.045 (4)	131 (4)
O8—H8...O11 ^{ix}	0.81 (2)	2.01 (4)	2.693 (4)	142 (6)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1, -y+1, -z$; (iii) $-x, -y+1, -z$; (iv) $x-1, y+1, z$; (v) $x, y+1, z$; (vi) $-x+1/2, y+1/2, -z+1/2$; (vii) $x+1/2, -y+3/2, z-1/2$; (viii) $-x+3/2, y+1/2, -z+1/2$; (ix) $x-1, y, z$; (x) $x-1/2, -y+3/2, z+1/2$; (xi) $x-1/2, -y+1/2, z+1/2$; (xii) $-x+1/2, y-1/2, -z+1/2$.