Supramolecular polymers of two novel 4-substituted-1,2,4-triazolate complexes: $[Cd(^pCltrz)_2(NCS)_2(H_2O)_2]$ and $[Cu(4\text{-}atrz)_4(Cl)_{0.5}(H_2O)_{0.5}]\cdot(ClO_4)_{1.5}$ (^{p}Cltrz: 4-(*p*-chlorophenyl)-1,2,4-triazole; 4-atrz: 4-amino-1,2,4-triazole)

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The synthesis and structural characterisation of two novel complexes of 4-substituted-1,2,4-triazoles, namely $[Cd(^pCltrz)_2(NCS)_2(H_2O)_2]$ (**1**) and $[Cu(4\text{-}atrz)_4(Cl)_{0.5}(H_2O)_{0.5}]\cdot(ClO_4)_{1.5}$ (**2**), are described. Elemental analysis, IR spectra and X-ray crystal structure analysis were carried out to determine the compositions and crystal structures of two compounds. The cadmium atom in **1** has a distorted octahedral coordination and forms one-dimensional chains via hydrogen bonding contacts. **2** has a distorted pyramid environment at the copper atom and a unique double-layer supramolecular structure connected via hydrogen bonds.

Keywords: 4-substituted-1,2,4-triazolate complexes, $[Cd(^pCltrz)_2(NCS)_2(H_2O)_2]$, $[Cu(4\text{-}atrz)_4(Cl)_{0.5}(H_2O)_{0.5}]\cdot(ClO_4)_{1.5}$

The design and self-assembly of metal compounds into one-, two- and three-dimensional supramolecular architectures are currently attracting considerable attention for potential applications.[1-5] The systems self-assembled by weak interactions play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organisation of molecules in supramolecular chemistry. In particular, hydrogen-bond systems are important in the crystal engineering of nonlinear optical, magnetic and conducting materials.[6-10] However, the number of studies dealing with 4-substituted-l,2,4-triazole ligands complexes is still rather limited. Thus, further research on the geometry and structures of triazole-metal compounds is of great necessity. In this contribution, we succeeded in obtaining two novel complexes with two 4-substituted-l,2,4-triazole ligands, namely $[Cd(^pCltrz)_2(NCS)_2(H_2O)_2]$ (**1**) and $[Cu(4\text{-}atrz)_4\ (Cl)_{0.5}(H_2O)_{0.5}]\cdot(ClO_4)_{1.5}$ (**2**), respectively [^{p}Cltrz: 4-(*p*-chlorophenyl)-1,2,4-triazole; 4-atrz: 4-amino-1,2,4-triazole]. The X-ray investigations show that **1** and **2** form, via hydrogen-bonding, one-dimensional and double-layer two-dimensional structures, respectively. Herein, we report the synthesis and structural characterisation of **1** and **2**.

The crystal structure of $[Cd(^pCltrz)_2(NCS)_2(H_2O)_2]$ (**1**) (Fig. 1) consists of two ^{p}Cltrz ligands, two thiocyanate groups, two water molecules and one central cadmium ion. The Cd(II), which is surrounded by four nitrogen atoms in equatorial positions and two oxygen atoms, has distorted octahedral coordination. The terminal SCN groups are N-bonded and the two Cd–N–C angles are 148.7(4) and 130.3(4)°, respectively. The triazole rings are planar within experimental error. The Cd–O axial distances (2.300(3) and 2.309(3) Å) and the equatorial Cd–N bond lengths (2.262(4), 2.323(4) and 2.342(3) Å) agree well with the values in the literature for similar slightly distorted octahedral coordination of cadmium ions. The complexes are associated in chains by pairs of hydrogen bonds involving the H-bond donor N7AD of the triazole rings and the H-bond acceptor O1AA of coordinated water molecules as shown in Fig. 2.

The ORTEP drawing of **2** with the atomic numbering scheme is shown in Fig. 3. The copper atom in **2** is coordinated via four triazole nitrogen atoms and one chloride or oxygen atom (the disorder site of oxygen and chloride atom is 50%) to form a distorted pyramid. In the space structure, there is a closely fourfold axis passing through the metal atom and the chloride atom (we descript the chloride or oxygen atom as chloride atom only), consequently, the molecule has a nearly C_4 symmetry. The average Cu(1)–N bond length is observed to be 1.994 Å while the Cu(1)–Cl(1) bond length is 2.299(5) Å. The chloride atom is connected by hydrogen bonding with four nitrogen atoms of four amino groups in different triazole ligands (see Fig. 4). The separation of Cu1E and O4AA (2.634 Å) indicates the existence weak interaction between copper and oxygen atoms.

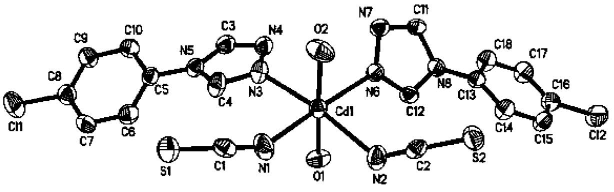

Fig. 1 The molecular structure and atom-labelling scheme of **1**.

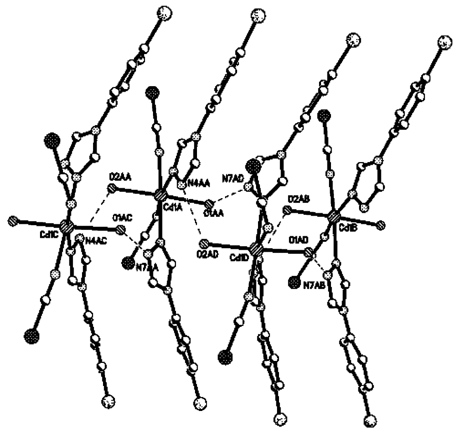

Fig. 2 The molecule packing of **1**.

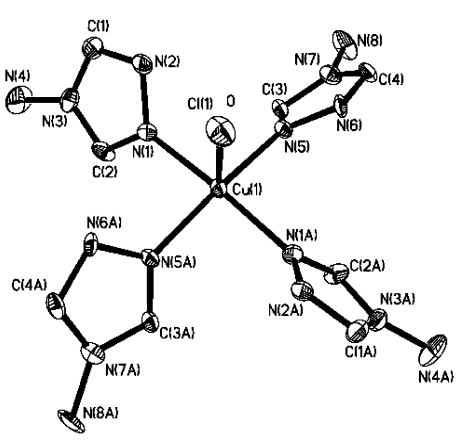

Fig. 3 The molecular structure and atom-labelling scheme of **2**, omitting the uncoordinated perchlorate ions for clarity.

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The molecule packing of compound **2** is shown in Fig. 5. The ClO_4^- anions in **2** contain disordered oxygen atoms. The nitrogen atoms of four amino groups in different triazole ligands of each molecule are connected by hydrogen bonding with four chloride atoms of four other molecules to form a unique double-plane 2D structure. These are also hydrogen bonds between the oxygen atoms of ClO_4^- and the amino groups of triazole.

In both complexes, intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur between nitrogen atoms of triazole rings and other atoms (oxygen and chloride atoms) to form mutli-dimensional structures. **1** has one-dimensional chain while **2** has double-layer two-dimensional planes. To the best of our knowledge, the supramolecular structure shown by **2** in triazole-metal compounds is unique. By blocking the N4 donor position through substitution, only the N1 monodentate and the N1N2-didentate coordination modes are possible. In the present contribution, 4-substituted-l,2,4-triazole ligands (^{p}Cltrz and 4-atrz) are monodentate in both complexes.

Experimental

^{p}Cltrz and 4-atrz were obtained as described in the literature. [11] The two ligands have been characterised by elemental analyses and NMR spectroscopy. Metal salts and other chemical reagents were obtained from commercial sources and used without further purification.

The complex **1** was prepared by using the H-tube method. ^{p}Cltrz (0.2 mmol) was placed in one side of the H-tube, and then $Cd(SCN)_2{\cdot}5H_2O$ (0.1 mmol) was added into the other side of the H-tube, ethanol–water(1:1) solution (10 ml) was slowly added into the tube and then the nozzle was sealed with tape. After three weeks, colourless crystals of **1** suitable for X-ray analysis were obtained. Yield: 36%. Elemental analyses result found (%): C 34.6, H 2.7, N 18.0. Calculated for $C_{18}H_{16}CdCl_2N_8O_2S_2$ (%): C 34.6, H 2.6, N 18.0.

The complex **2** was prepared by a different method. A methanol mixed solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.1 mmol) and NaCl (0.1 mmol) was slowly added to an methanol solution of 4-atrz (0.6 mmol). After stirring for 5 h at room temperature, the green solution was filtered and slowly evaporated in a refrigerator. After two weeks, green plate-like crystals of **2** suitable for X-ray analysis were obtained. Yield: 18%. Elemental analyses result found (%): C 16.8, H 2.7, N 38.6. Calculated for $C_8H_{17}Cl_2CuN_{16}O_{6.5}$ (%): C 16.7, H 3.0, N 38.9.

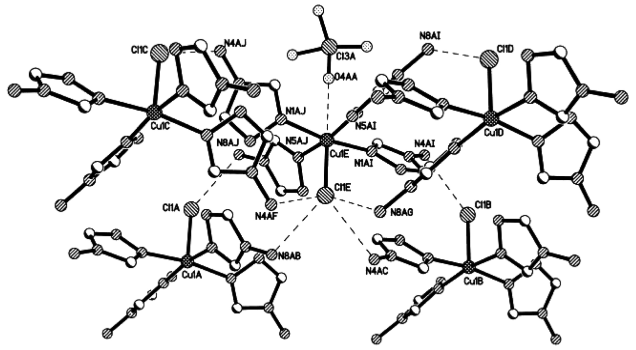

Fig. 4 View of the hydrogen bonds in **2**.

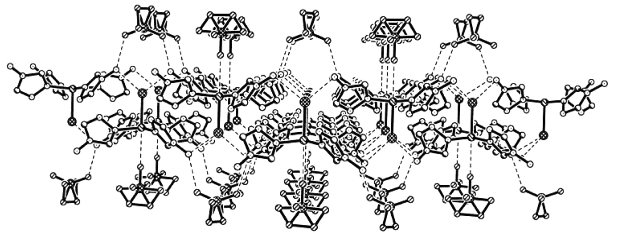

Fig. 5 The molecule packing of **2**.

X-ray diffraction data were collected on a Bruker SMART 1000 CCD detector with graphite-monochromatised Mo–Kα radiation (λ = 0.71073 Å) for compounds **1** and **2**. The structures were solved by direct method using the program SHELXS 97 [12] and Fourier difference techniques. Refinement was by the full-matrix least-squares method on F^2 using SHELXL 97.[13] Crystal data and structure refinements are summarised in Table 1. Selected bond lengths and angles are given in Table 2.

Infrared spectra (KBr pellets) were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 cm^{-1}. NMR spectra were recorded using Mercury VX300M. In the IR spectra, the typical stretching frequencies of 1,2,4-triazole ligands are 3133m, 1531s,

Table 1 Data collection and processing parameters for **1** and **2**

	$[Cd({}^{p}Cltrz)_2(NCS)_2(H_2O)_2]$ (**1**)	$[Cu(4\text{-}atrz)_4(Cl)_{0.5}(H_2O)_{0.5}]{\cdot}(ClO_4)_{1.5}$ (**2**)
Empirical formula	$C_{18}H_{16}CdCl_2N_8O_2S_2$	$C_8H_{17}Cl_2CuN_{16}O_{6.5}$
Formula weight	623.81	575.82
Temperature (K)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	P_{212121}	$C_{2/c}$
a (Å)	8.302(3)	11.159(10)
b (Å)	8.415(3)	18.027(10)
c (Å)	33.844(13)	11.071(7)
β (°)		90.751(17)
Volume	2364.2(15) Å^3	2227(3) Å^3
Z	4	4
Density (calculated) (mg/m^3)	1.753	1.717
Absorption coefficient(mm^{-1})	1.360	1.287
F(000)	1616	1168
Crystal size (mm^3)	0.43 × 0.15 × 0.13	0.30 × 0.25 × 0.20
θ range for data collection (°)	2.41–25.03	2.15–26.48
Limiting indices	$-9 \le h \le 9$ $-10 \le k \le 8$ $-40 \le l \le 34$	$-11 \le h \le 13$ $-22 \le k \le 16$ $-13 \le l \le 12$
Reflections collected	12479	4792
Independent reflections	4153 [*R*(int) = 0.0352]	2182 [*R*(int) = 0.1535]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. transmission	0.8430 and 0.5924	0.7829 and 0.6988
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4153 / 6 / 314	2182 / 7 / 188
Goodness-of-fit on F^2	0.996	0.905
*R*1, *wR*2 [$I>2\sigma$ (I)]	0.0319, 0.0561	0.0712, 0.1195
*R*1, *wR*2 (all data)	0.0388, 0.0577	0.2292, 0.1620
Largest diff. peak and hole	0.574 and –0.418 e·Å^{-3}	0.367 and –0.348 e·Å^{-3}

[a]: $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2)^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.0000P]$, $P = (Fo^2 + 2Fc^2)/3$ for **1** and $w = 1/[\sigma^2(Fo^2) + (0.0587P)^2 + 0.0000P]$, $P = (Fo^2 + 2Fc^2)/3$ for **2**.

Table 2 Selected bond lengths (Å) and angles (°) for (**1**) and (**2**)

$[Cd(^{p}Cltrz)_2(NCS)_2(H_2O)_2]$ (**1**)		$[Cu(4\text{-}atrz)_4(Cl)_{0.5}(H_2O)_{0.5}]\cdot(ClO_4)_{1.5}$ (**2**)	
Cd(1)–N(1)	2.262(4)	Cu(1)–N(5)#1	1.986(5)
Cd(1)–O(2)	2.300(3)	Cu(1)–N(5)	1.986(5)
Cd(1)–O(1)	2.309(3)	Cu(1)–N(1)#1	2.002(6)
Cd(1)–N(2)	2.323(4)	Cu(1)–N(1)	2.002(6)
Cd(1)–N(6)	2.342(3)	Cu(1)–Cl(1)	2.299(5)
Cd(1)–N(3)	2.342(4)		
N(1)–Cd(1)–O(2)	84.49(17)	N(5)#1–Cu(1)–N(5)	170.1(4)
N(1)–Cd(1)–O(1)	98.86(16)	N(5)#1–Cu(1)–N(1)#1	89.8(2)
O(2)–Cd(1)–O(1)	176.57(12)	N(5)–Cu(1)–N(1)#1	89.4(2)
N(1)–Cd(1)–N(2)	88.64(13)	N(5)#1–Cu(1)–N(1)	89.4(2)
O(2)–Cd(1)–N(2)	94.85(18)	N(5)–Cu(1)–N(1)	89.8(2)
O(1)–Cd(1)–N(2)	85.98(17)	N(1)#1–Cu(1)–N(1)	170.5(4)
N(1)–Cd(1)–N(6)	175.84(15)	N(5)#1–Cu(1)–Cl(1)	94.96(19)
O(2)–Cd(1)–N(6)	93.84(15)	N(5)–Cu(1)–Cl(1)	94.96(19)
O(1)–Cd(1)–N(6)	82.86(14)	N(1)#1–Cu(1)–Cl(1)	94.77(19)
N(2)–Cd(1)–N(6)	87.70(12)	N(1)–Cu(1)–Cl(1)	94.77(19)
N(1)–Cd(1)–N(3)	89.76(14)		
O(2)–Cd(1)–N(3)	94.39(14)		
O(1)–Cd(1)–N(3)	84.95(13)		
N(2)–Cd(1)–N(3)	170.4(2)		
N(6)–Cd(1)–N(3)	94.17(11)		
C(1)–N(1)–Cd(1)	148.7(4)		
C(2)–N(2)–Cd(1)	130.3(4)		

1484vs, 885vs, 641vs cm^{-1} in **1** and 3135m, 1496vs, 880vs, 634vs cm^{-1} in **2**, respectively. The IR spectrum of the complex **1** confirms the $\nu_{s(SCN)}$ at 2100 cm^{-1}. The IR spectrum of the complex **2** confirms the existence of ClO_4^- at 1113 cm^{-1}.

The CCDC numbers of **1** and **2** are 212757 and 196208, respectively.

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