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Copper(II) and cadmium(II) isothiocyanate coordination polymers with 4,4′-bi-1,2,4-triazole

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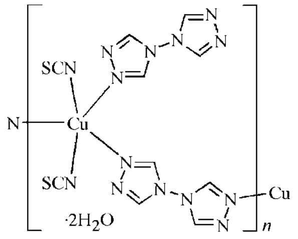
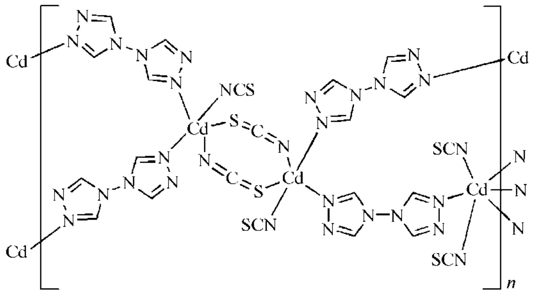
The coordination polymers *catena*-poly[[[(4,4′-bi-1,2,4-triazole-κN^1)bis(thiocyanato-κN)copper(II)]-μ-4,4′-bi-1,2,4-triazole-$\kappa^2 N^1$:$N^{1'}$] dihydrate], $\{[Cu(NCS)_2(C_4H_4N_6)_2]\cdot 2H_2O\}_n$, (I), and poly[tetrakis(μ-4,4′-bi-1,2,4-triazole-$\kappa^2 N^1$:$N^{1'}$)bis(μ-thiocyanato-$\kappa^2 N$:S)tetrakis(thiocyanato-κN)tricadmium(II)], $[Cd_3(NCS)_6(C_4H_4N_6)_4]_n$, (II), exhibit chain and two-dimensional layer structures, respectively. The differentiation of the Lewis acidic nature of Cu^{II} and Cd^{II} has an influence on the coordination modes of the triazole and thiocyanate ligands, leading to topologically different polymeric motifs. In (I), copper ions are linked by bitriazole *N*:*N*′-bridges into zigzag chains and the tetragonal–pyramidal CuN_5 environment is composed of two thiocyanate N atoms and three triazole N atoms [basal Cu—N = 1.9530 (18)–2.0390 (14) Å and apical Cu—N = 2.2637 (15) Å]. The structure of (II) contains two types of crystallographically unique Cd^{II} atoms. One type lies on an inversion center in a distorted CdN_6 octahedral environment, with bitriazole ligands in the equatorial plane and terminal isothiocyanate N atoms in the axial positions. The other type lies on a general position and forms centrosymmetric binuclear $[Cd_2(\mu\text{-NCS-}\kappa^2 N\text{:}S)_2(NCS)_2]$ units (tetragonal–pyramidal CdN_4S coordination). *N*:*N*′-Bridging bitriazole ligands link the Cd centers into a flat (4,4)-network.

Comment

The growing interest in the structural design of M^{II}–bi-1,2,4-triazole coordination polymers (where M = Fe^{II}, Cu^{II} and Cd^{II}) has been dictated by their importance in the fields of magnetism and fluorescence (Janiak, 2000). The bitopic bitriazoles propagate local coordination environments around either discrete metal ions or polynuclear secondary building units as nodes, forming metal–organic frameworks (MOFs). The adjacent N atoms (N1 and N2) in 1,2,4-triazole derivatives are well suited for binding together transition metal cations, leading to characteristic polynuclear clusters, *viz.* dimers (Drabent *et al.*, 2004), linear (Liu *et al.*, 1999) and triangular trimers (Virovets *et al.*, 1997), *etc.* Recently, for the Cu^{II}–btr–X^- systems (X = Cl and Br; btr is 4,4′-bi-1,2,4-triazole), we have demonstrated how such cluster motifs may be rationally integrated in the MOFs (Lysenko *et al.*, 2006, 2007). Obviously, the nature of the anion is a crucial factor that determines the resulting structure and net topology of the M^{II}–btr polymers. In this context, a very interesting situation could be realized in the case of pseudohalide anions, *e.g.* NCS^-, that are complementary to a short triazole linker, and such a combination of neutral and anionic bridges can support the formation of triangular Cu^{II} $\{[Cu_3(\mu_3\text{-OH})(\mu_2\text{-}L)_4(H_2O)(NCS)_3](ClO_4)_2\cdot H_2O$; Liu *et al.*, 2003$\}$ and linear trinuclear Cd^{II} cores $\{[\{Cd_3(\mu_2\text{-}L)_4(\mu_2\text{-NCS})_2\}(\mu_2\text{-NCS})_2(NCS)_2]$; L is 4-amino-3,5-dimethyltriazole; Yi *et al.*, 2004$\}$. We report here the crystal



(I)



(II)

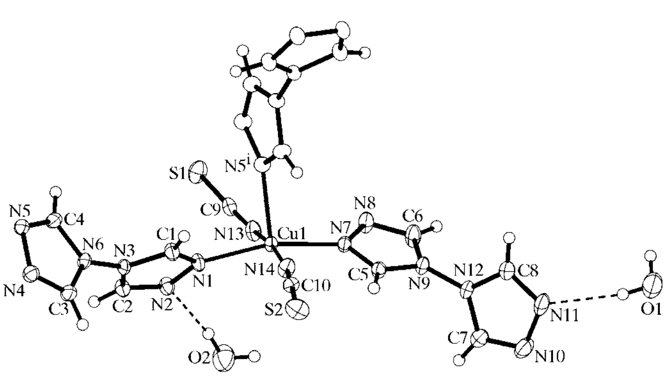


Figure 1
A portion of the structure of (I), showing the atom-labeling scheme and the copper coordination environment. Displacement ellipsoids are drawn at the 40% probability level. The dashed line represents an intermolecular hydrogen bond. [Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.]

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structures of two new coordination polymers, *viz*. $[Cu(NCS)_2(btr)_2]\cdot 2H_2O$, (I), and $[Cd_3(NCS)_6(btr)_4]$, (II), that build on these ideas.

In (I), the Cu1 centers are located in general positions and possess a distorted tetragonal–pyramidal environment of five N atoms. The basal sites of the pyramid are occupied by two terminal *trans*-coordinated isothiocyanate groups and one N atom each from one terminal and one $N^1,N^{1'}$-bidentate btr molecules, while the apical position is occupied by the other N atom of a symmetry-related bidentate btr ligand (Fig. 1 and Table 1). The $Cu-N_{NCS}$ bond lengths are slightly shorter than those observed in the similar five-coordinate complexes $Cu(NCS)_2$(3-methylpyridine)$_3$ [1.973 (9) and 2.194 (13) Å] and $Cu(NCS)_2$(3,4-dimethylpyridine)$_3$ [1.981 (13) and 2.215 (17) Å] (Kabesova & Koziskova, 1989).

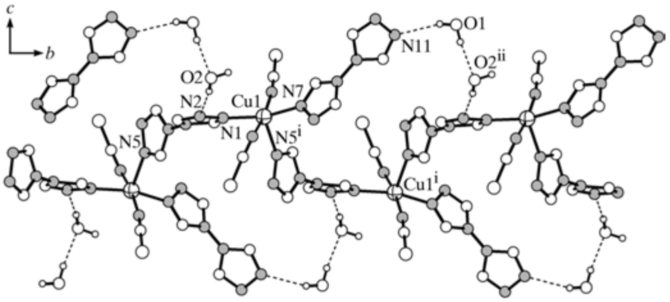

Figure 2
A view of the zigzag coordination chain in the structure of (I), showing the bridging function of the ligand and the principal hydrogen bonding (projection on the *bc* plane). The bitriazole H atoms have been omitted for clarity and N atoms are shaded grey. [Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y+1, z$.]

The *N*,*N*′-bidentate btr molecules link adjacent Cu atoms [related by the symmetry operation $(-x, y+\frac{1}{2}, -z+\frac{3}{2})$] at a distance of 9.1198 (5) Å. Their *cis* location around the metal center leads to the formation of zigzag $[Cu(\mu_2\text{-btr})]_n^{2n+}$ chains running along the *b* axis (Fig. 2), with corresponding $Cu\cdots Cu\cdots Cu$ angles of 86.81 (1)° and separations between the translating units [related by $(x, y+1, z)$] of 12.5332 (9) Å. Neighboring chains, which are related by translation along the *a* axis, afford tight packing with a closest $Cu1\cdots Cu1(x+1, y, z)$ distance of 6.9047 (4) Å. The $N^1,N^{1'}$-bidentate coordination mode of btr is widely found (Vreugdenhil *et al.*, 1985); however, the polymeric motif with two types of mono- and bidentate-coordinated btr molecules similar to (I) is uncommon. The only structural precedent is $[Mn(NCS)(\mu_2\text{-btr})(btr)_2(H_2O)]NCS$ (Zilverentant *et al.*, 1998).

The uncoordinated water molecules in (I) are involved in hydrogen-bonding interactions with one another [$O1\cdots O2^{ii}$ = 2.914 (3) Å; symmetry code: (ii) $x, y+1, z$; Fig. 2]. This 'dimer' can be considered as a donor of two hydrogen bonds towards two btr molecules [$O1\cdots N11$ = 2.997 (3) Å and $O2\cdots N2$ = 2.933 (3) Å] with one weak hydrogen bond towards the S atom of an NCS^- anion [$O2\cdots S2^{iii}$ = 3.331 (2) Å; symmetry code: (iii) $x+1, y, z$; Table 2] (Desiraju & Steiner, 1999). These interactions lead to interconnection of the coordination chains into two-dimensional hydrogen-bonded layers aligned parallel to the *bc* plane.

The Lewis softness of the Cd^{2+} centers in (II) and their higher affinity towards NCS^- anions, either as N- or S-atom

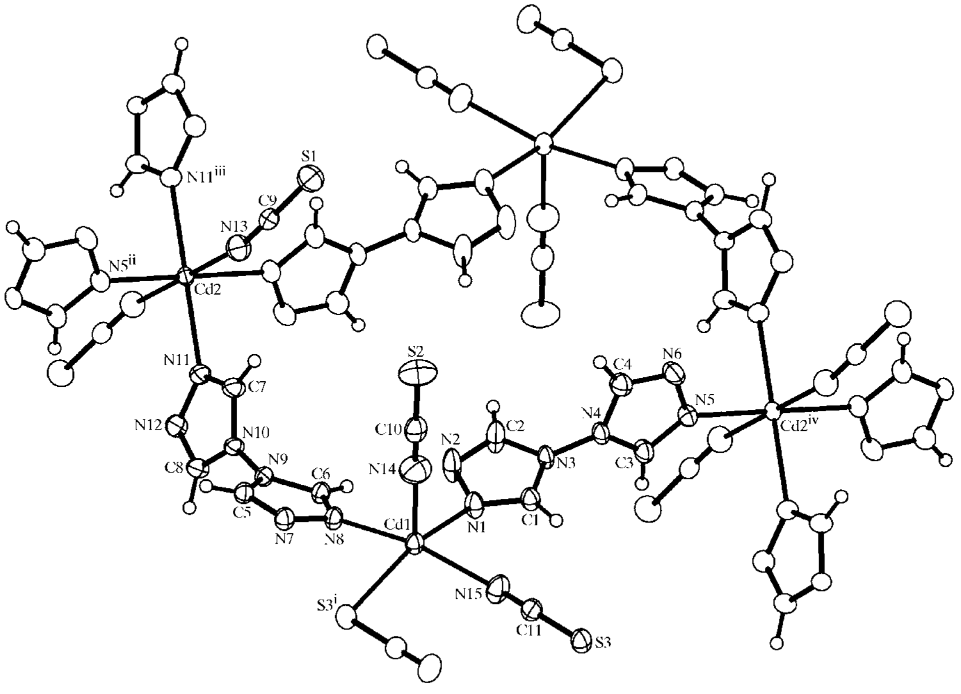

Figure 3
A portion of the structure of (II), showing the atom-labeling scheme and the cadmium coordination environments. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, y, z-1$; (iii) $-x, -y, -z$; (iv) $x, y, z+1$.]

donors, effects the formation of an even more complicated polymeric motif as compared with the copper(II) complex. The structure of (II) involves two types of coordination environments (Fig. 3). Two equivalent Cd1 ions [related by the symmetry operation ($-x + 2, -y + 1, -z + 1$)] are linked by a pair of thiocyanate *N*:*S*-bridges into centrosymmetric dimers, and the distorted tetragonal–pyramidal N_4S environment of the Cd1 center is completed by two triazole N-atom donors with an N atom of a terminal thiocyanate group in the apical position (Fig. 4). Within these double bridged $Cd_2(\mu_2\text{-NCS})_2$ dimers, the Cd$\cdots$Cd distance [5.7044 (9) Å] is similar to those observed in the related complex $[N(C_3H_7)_4][Cd(\mu_2\text{-NCS})_2\text{-}(NCS)]$ (5.715 and 5.856 Å; Taniguchi & Ouch, 1989). The eight-membered $Cd_2(\mu_2\text{-NCS})_2$ ring possesses a 'chair' conformation [the displacement of atom Cd1 out of the $(NCS)_2$ plane is 0.544 Å], and two terminal NCS^- anions are attached to the Cd1 ions at the opposite sides of the metallocycle. This $Cd_2(\mu_2\text{-NCS})_2(NCS)_2$ arrangement is rarely found and has only two precedents, in $[\{Cd_3(\mu_2\text{-tr})_4(\mu_2\text{-Cl})_2\}\text{-}(\mu_2\text{-NCS})_2(NCS)_2]\cdot 2H_2O$ (tr is 4-amino-3,5-diethyltriazole; Yi *et al.*, 2004) and $[N(C_3H_7)_4][Cd(\mu_2\text{-NCS})_2(NCS)]$ (Taniguchi & Ouch, 1989), with octahedral and tetragonal–pyramidal metal atoms, respectively.

The coordination environment of the second unique Cd ion is much simpler. Atom Cd2 is located on a center of inversion and has a slightly distorted octahedral environment involving four triazole N-atom donors in the equatorial plane and two isothiocyanate groups in the axial positions (Table 3).

Each $(Cd1)_2(\mu\text{-NCS})_2$ unit and discrete Cd2 ion coordinates four triazole groups and this predetermines parity of their structural functions; both of them (in a 1:1 proportion) provide four-connected nodes for a planar (4,4)-network, and the corresponding diagonal Cd2$\cdots$Cd2^{iv} [symmetry code: (iv) $x, y, z + 1$] separations are 13.836 Å (*c* parameter of the unit cell) (Figs. 3 and 4). Adjacent layers are shifted and stacked at a distance of 5.20 Å. The terminal coordinating isothiocyanate groups containing atoms S1 and S2 are directed inside the pores of the adjacent layer at ($x + 1, y, z$) to afford interdigitation of the successive nets.

In both structures, the btr molecules display an almost orthogonal orientation of the two triazole groups, which does not depend on the coordination mode of the ligand. The dihedral angles between the planes of the triazole heterocycles lie in the range 77.58 (4)–89.99 (4)°, in good agreement with those reported for free 4,4′-bi-1,2,4-triazole [88.12 (1)°; Domiano, 1977].

These results demonstrate that the btr molecule in combination with the nucleophilic isothiocyanate anion (*N*-terminal and *N*,*S*-bidentate roles) as coligand adopts monodentate and $N^1,N^{1'}$-bidentate coordination behavior toward Cu^{II} and Cd^{II}, leading to the formation of low-dimensional coordination polymers.

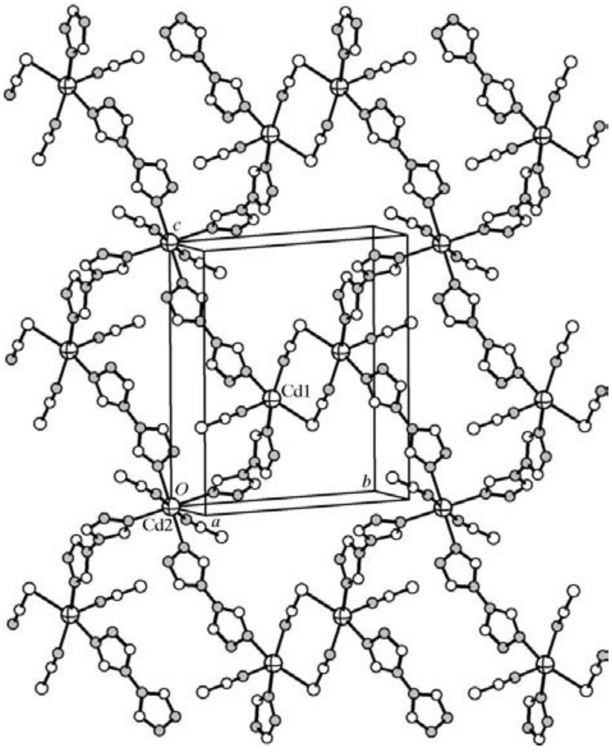

Figure 4
The two-dimensional network in the structure of (II) contains two types of nodal units, *viz*. $[(Cd1)_2(\mu\text{-NCS})_2(NCS)_2]$ and Cd2, linked by N^1:$N^{1'}$-bidentate bitriazole bridges.

Experimental

All materials were of reagent grade and were used as received. The btr ligand was prepared according to a reported procedure (Bartlett *et al.*, 1967). The precipitate obtained by mixing aqueous $CuSO_4\cdot 5H_2O$ (0.0250 g, 0.100 mmol), CsSCN (0.0382 g, 0.200 mmol) and btr (0.0136 g, 0.100 mmol) solutions was recrystallized from water to afford green prisms of (I) (yield 83%). Evaporation of an aqueous solution (3 ml) of $Cd(SCN)_2$ (0.0457 g, 0.200 mmol) and btr (0.0136 g, 0.100 mmol) in a desiccator over $CaCl_2$ for a few days afforded colorless prisms of (II) (yield 98%).

Compound (I)

Crystal data

$[Cu(NCS)_2(C_4H_4N_6)_2]\cdot 2H_2O$
$M_r = 488.00$
Orthorhombic, $P2_12_12_1$
$a = 6.9047$ (4) Å
$b = 12.5332$ (9) Å
$c = 21.8652$ (18) Å
$V = 1892.2$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.42$ mm^{-1}
$T = 213$ (2) K
$0.20 \times 0.18 \times 0.18$ mm

Data collection

Stoe IPDS diffractometer
18528 measured reflections
4417 independent reflections
4019 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.051$
$S = 0.95$
4417 reflections
262 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 1806 Friedel pairs
Flack parameter: -0.001 (8)

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N13	1.9530 (18)	Cu1—N1	2.0390 (14)
Cu1—N14	1.9678 (18)	Cu1—N5^{i}	2.2637 (15)
Cu1—N7	2.0124 (15)		
N13—Cu1—N14	171.45 (8)	N13—Cu1—N1	88.87 (7)
N13—Cu1—N7	91.90 (7)	N14—Cu1—N1	87.91 (7)
N14—Cu1—N7	89.27 (7)	N7—Cu1—N1	165.65 (7)
C1—N3—N6—C4	88.1 (3)	C6—N9—N12—C8	85.2 (3)

Symmetry code: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Compound (II)

Crystal data

$[Cd_3(NCS)_6(C_4H_4N_6)_4]$
M_r = 1230.21
Triclinic, $P\overline{1}$
a = 7.0920 (10) Å
b = 10.4867 (18) Å
c = 13.836 (2) Å
α = 87.440 (18)°
β = 81.158 (16)°
γ = 82.847 (11)°
V = 1008.5 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.94 mm^{-1}
T = 298 (2) K
0.40 × 0.25 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.510, T_{max} = 0.800
5237 measured reflections
4853 independent reflections
3813 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.074
S = 1.05
4853 reflections
277 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1W···N11	0.85	2.21	2.997 (3)	154
O1—H2W···O2^{ii}	0.85	2.08	2.914 (3)	166
O2—H3W···S2^{iii}	0.85	2.52	3.331 (2)	159
O2—H4W···N2	0.85	2.10	2.933 (3)	166

Symmetry codes: (ii) $x, y+1, z$; (iii) $x+1, y, z$.

All H atoms were located in difference maps and included as riding atoms, with O—H distances constrained to 0.85 Å and C—H distances constrained to 0.94 Å, and with U_{iso}(H) values of 1.2U_{eq}(C) and 1.5U_{eq}(O).

For (I), data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; software used to prepare material for publication: *WinGX* (Farrugia, 1999). For (II), data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999).

Table 3
Selected geometric parameters (Å, °) for (II).

Cd1—N14	2.178 (4)	Cd1—S3^{i}	2.6142 (10)
Cd1—N15	2.261 (3)	Cd2—N13	2.256 (3)
Cd1—N8	2.303 (2)	Cd2—N5^{ii}	2.347 (3)
Cd1—N1	2.335 (3)	Cd2—N11	2.386 (3)
N14—Cd1—N15	101.05 (14)	N8—Cd1—S3^{i}	85.87 (7)
N14—Cd1—N8	98.51 (12)	N1—Cd1—S3^{i}	159.25 (8)
N15—Cd1—N8	159.79 (13)	N13—Cd2—N5^{ii}	91.38 (11)
N14—Cd1—N1	98.97 (14)	N5^{ii}—Cd2—N11	85.15 (9)
N15—Cd1—N1	82.24 (10)	N13—Cd2—N11^{iii}	91.91 (11)
N8—Cd1—N1	89.75 (9)		
C6—N9—N10—C7	−83.6 (4)		

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3120). Services for accessing these data are described at the back of the journal.

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