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Novel Triazole-Bridged Cadmium Coordination Polymers Varying from Zero- to Three-Dimensionality

Long Yi, Bin Ding, Bin Zhao, Peng Cheng,* Dai-Zheng Liao, Shi-Ping Yan, and Zong-Hui Jiang

Department of Chemistry, Nankai University, Tianjin 300071, China

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Cadmium salts with different triazole ligands have led to a series of novel triazole–cadmium compounds varying from zero- to three-dimensionality. $[Cd_2(deatrz)_2(H_2O)Br_4]$ (**1**) (deatrz = 3,5-diethyl-4-amino-1,2,4-triazole) is a zero-dimensional complex which uses a triazole ligand together with μ-OH_2 as bridges to form a 1D chain via hydrogen-bonding contacts. $\{[Cd_3(deatrz)_2Cl_6(H_2O)_2]\cdot 2H_2O\}_n$ (**2**), $\{[Cd(dmtrz)Cl_2]\cdot 1.5H_2O\}_n$ (**3**) (dmtrz = 3,5-dimethyl-1,2,4-triazole), and $\{[Cd_3(deatrz)_4Cl_2(SCN)_4]\cdot 2H_2O\}_n$ (**4**) are polymeric 1D chains. **2** and **4** were constructed via trinuclear cadmium units bridged by triazole ligands and chloride atoms, while **3** consists of μ_2-Cl, μ_3-Cl, and triazole bridges, cross-linked by hydrogen bonding to give a 3D framework. $\{[Cd_3(dmatrz)_4(SCN)_6]\}_n$ (**5**) (dmatrz = 3,5-dimethyl-4-amino-1,2,4-triazole) shows a two-dimensional structure whose fundamental units are trinuclear metal cations bridged via triazole ligands. The complex $\{[Cd(dmtrz)(SCN)_2]\}_n$ (**6**) is the first three-dimensional example in N1,-N2-didentate-bridged triazole–metal compounds. Six complexes exhibit six types of bridging modes of N1,N2-triazole in combination with single-atom bridges. **2**, **4**, and **5** are the unprecedented examples of polymeric chains and planes constructed via trinuclear metal ion clusters, whereas **3** is the first example of the μ_3-Cl bridging mode in triazole–metal complexes. We have briefly discussed the variety of dimensionalities based on the tuning of different organic ligands and anions.

Introduction

The study of metal coordination polymers has gained great recognition as an important interface between synthetic chemistry and materials science, and provides a solid foundation for understanding how molecules can be organized and how functions can be achieved. Thus, structural design or modification of the coordination framework has become a very active field in crystal engineering.[1−12] The current topical areas focus on the construction of supramolecular frameworks with novel topology through metal-based coordination and on the crystal engineering of molecular architectures organized by coordinate covalent bonds or supramolecular contacts (such as hydrogen bonding, $\pi-\pi$ interactions, etc.).[13−20] On the other hand, coordination polymers of one-, two-, and three-dimensional infinite frameworks involving cadmium(II) ions have been the

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* Author to whom correspondence should be addressed. E-mail: pcheng@nankai.edu.cn.

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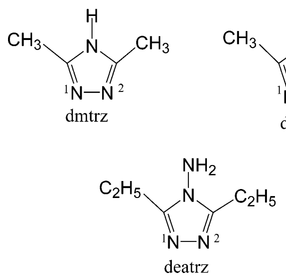
subject of great interest in recent years owing to their potential applications in catalysis, optical properties evolution, clathration, etc.[21−25] The d^{10} configuration and softness of cadmium(II) permit a wide variety of geometries and coordination numbers. The coordination polymers of cadmium(II) have been exploited using organic ligands as well as anions, e.g., Cl^-, Br^-, I^-, SCN^-, N_3^-, $SeCN^-$,[25−34] etc., which are an essential part of the coordination polyhedra. The organic ligands, as well as the anions, are observed to control the structural dimensionalities and stereochemistry of a cadmium(II) center.[17,18] To develop further our understanding of supramolecular architecture construction, it is challenging to continue the investigations on the effect of organic ligands and anions in fabricating multidimension polymers.

The field of molecular materials has been known as a rapid development in recent years, and molecular-based compounds exhibiting interesting magnetic and luminescent properties have been described.[35−38] One of the requirements to observe such macroscopic properties is to create some interactions between the molecular units or the active sites within the crystal lattice. 1,2,4-Triazole and, in particular, its derivatives are very interesting as bridging ligands. However, not many compounds in this field have been described, and only a few crystal structures are known, especially for triazole−metal coordination polymers.[38] To the best of our knowledge, there are only four triazole−cadmium coordinated polymers in which the X-ray single-crystal structures have been determined up until now.[39−42]

Chart 1



To develop further our understanding of the interactions of triazole ligands with metals, further research on the geometry and structures of triazole−metal compounds is of great necessity.

In this study, we prepared several triazole ligands, investigated their coordination abilities with cadmium salts, and isolated a series of novel cadmium−triazole complexes. The three triazole ligands we chose in this study, such as 3,5-dimethyl-1,2,4-triazole (dmtrz), 3,5-dimethyl-4-amino-1,2,4-triazole (dmatrz), and 3,5-diethyl-4-amino-1,2,4-triazole (deatrz), are structurally closely related to each other and have the same N1,N2-didentate bridging modes (Chart 1).

To obtain more information on supramolecular architecture construction and triazole−metal coordinated structures, herein we report six complexes which have a variety of zero-, one-, two-, and three-dimensional frameworks via tuning different triazole ligands and anions. The six complexes, namely, $[Cd_2(deatrz)_2(H_2O)Br_4]$ (**1**), $\{[Cd_3(deatrz)_2Cl_6(H_2O)_2]\cdot 2H_2O\}_n$ (**2**), $\{[Cd(dmtrz)Cl_2]\cdot 1.5H_2O\}_n$ (**3**), $\{[Cd_3(deatrz)_4Cl_2(SCN)_4]\cdot 2H_2O\}_n$ (**4**), $\{[Cd_3(dmatrz)_4(SCN)_6]\}_n$ (**5**), and $\{[Cd(dmtrz)(SCN)_2]\}_n$ (**6**), were revealed by single-crystal X-ray diffraction analysis. The unusual bridging modes in the six complexes were described and discussed in detail. The effects of ligand functionality and anion control were investigated within the cadmium−triazole system.

Experimental Section

Materials. The three triazole ligands were synthesized according to the literature method with some modifications of prolonging the reaction time at 180 °C to enhance the yields.[43] All other reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Bio-Rad FTS 135 spectrometer.

Preparations. $[Cd_2(deatrz)_2(H_2O)Br_4]$ (1). A mixture of $CdBr_2$ (0.20 mmol), deatrz (0.40 mmol), and water (10 mL) was stirred for 5 h and filtered. The filtrate was kept in a $CaCl_2$ desiccator. After a few days suitable single crystals were obtained for X-ray diffraction study, yield 21%. Anal. Calcd for $C_{12}H_{26}Br_4Cd_2N_8O$: C, 17.29; H, 2.85; N, 13.57. Found: C, 17.09; H, 3.08; N, 13.29. IR (KBr): ν = 3431.1m, 3361.6m, 3255.0m, 3205.33s, 3160.9w, 2979.6s, 2938.1s, 2877.4m, 2655.3w, 2122.7w, 1622.9s, 1581.6m,

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Table 1. Crystallographic Data and Structure Refinement for **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{12}H_{26}Br_4Cd_2N_8O$	$C_{12}H_{32}Cd_3Cl_6N_8O_4$	$C_4H_{10}CdCl_2N_3O_{1.5}$	$C_{28}H_{52}Cd_3Cl_2N_{20}O_2S_4$	$C_{22}H_{32}Cd_3N_{22}S_6$	$C_6H_7CdN_5S_2$
fw	842.83	902.36	307.45	1237.24	1134.26	325.69
temp (K)	298(2)	293(2)	298(2)	293(2)	293(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	Pbca	$P2(1)/c$
a (Å)	13.039(9)	9.726(4)	9.157(4)	8.657(7)	18.428(6)	13.210(7)
b (Å)	17.821(12)	15.656(6)	10.054(4)	11.312(10)	11.066(4)	11.465(6)
c (Å)	11.064(8)	9.988(4)	10.609(4)	13.068(11)	20.899(6)	14.506(8)
α (deg)			85.919(6)	73.947(14)		
β (deg)	92.388(12)	110.665(6)	85.103(5)	86.495(14)		92.743(8)
γ (deg)			82.677(5)	77.629(10)		
V (Å^3)	2569(3)	1423.1(9)	963.3(6)	1201.3(18)	4262(2)	2194(2)
Z	4	2	4	1	4	8
F(000)	1592	876	596	618	2232	1264
ρ (Mg/m^3)	2.174	2.106	2.120	1.710	1.768	1.972
abs coeff (mm^{-1})	7.895	2.818	2.780	1.651	1.824	2.339
no. of data/restraints/params	4190/0/244	2877/0/151	3268/0/211	3909/0/268	3755/12/252	3877/0/253
GOF	0.919	1.017	0.940	0.958	1.096	1.001
R1[a] ($I = 2\sigma(I)$)	0.0409	0.0274	0.0376	0.0648	0.0590	0.0279
wR2[a] (all data)	0.0582	0.0553	0.0891	0.1015	0.1329	0.0728

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

1549.7s, 1489.8m, 1457.1s, 1383.1m, 1329.2m, 1312.2m, 1281.9w, 1229.8s, 1059.6s, 957.4s, 795.2w, 762.1m, 736.8m, 722.1s, 703.5m, 530.4s, 420.7w cm^{-1}.

$\{[Cd_3(deatrz)_2Cl_6(H_2O)_2]\cdot 2H_2O\}_n$ (2). A mixture of $CdCl_2\cdot H_2O$ (0.20 mmol), deatrz (0.40 mmol), and water (10 mL) was stirred for 5 h and filtered. The filtrate was kept in a $CaCl_2$ desiccator. The resulting colorless solution slowly evaporated in air for over a week to give colorless polyhedral crystals of **2**, yield 68%. Anal. Calcd for $C_{12}H_{32}Cd_3Cl_6N_8O_4$: C, 15.67; H, 3.48; N, 12.21. Found: C, 15.96; H, 3.55; N, 12.41. IR (KBr): ν = 3552.8m, 3434.9m, 3305.5s, 3255.2m, 3205.4s, 3160.9m, 2979.4s, 2937.9s, 2877.2m, 2639.9w, 2121.4w, 1623.1s, 1582.3m, 1549.7s, 1489.8m, 1457.1s, 1382.8m, 1329.3m, 1314.4m, 1281.4m, 1229.9s, 1092.2w, 1059.5s, 958.1s, 794.4m, 761.9m, 736.8w, 721.9m, 703.8m, 530.0s, 420.7w cm^{-1}.

$\{[Cd(dmtrz)Cl_2]\cdot 1.5H_2O\}_n$ (3). A mixture of $CdCl_2\cdot H_2O$ (0.20 mmol), dmtrz (0.40 mmol), and water (10 mL) was stirred for 5 h and filtered. The filtrate was kept in a $CaCl_2$ desiccator. Clear colorless crystals were obtained from this solution, yield 72%. Anal. Calcd for $C_4H_{10}CdCl_2N_3O_{1.5}$: C, 15.89; H, 3.20; N, 13.48. Found: C, 15.61; H, 3.25; N, 13.66. IR (KBr): ν = 3530.4s, 3201.2m, 3056.7m, 3018.1m, 2934.9s, 2821.2s, 2778.8m, 2732.5m, 2665.4m, 2561.1m, 1582.8s, 1538.9s, 1458.7m, 1417.2s, 1392.3m, 1378.5s, 1339.2w, 1289.1w, 1242.8w, 1050.7s, 931.4m, 748.5s, 712.6m, 677.3m, 442.6s cm^{-1}.

$\{[Cd_3(deatrz)_4Cl_2(SCN)_4]\cdot 2H_2O\}_n$ (4). A mixture of $CdCl_2\cdot H_2O$ (0.20 mmol), NH_4SCN (0.40 mmol), deatrz (0.40 mmol), and water (10 mL) was stirred for 5 h and filtered. The filtrate was kept in a $CaCl_2$ desiccator. After the solution was allowed to stand at room temperature, complex **4** slowly crystallized, yield 35%. Anal. Calcd for $C_{28}H_{52}Cd_3Cl_2N_{20}O_2S_4$: C, 27.01; H, 4.28; N, 22.39. Found: C, 27.16; H, 4.20; N, 22.63. IR (KBr): ν = 3552.1m, 3433.9m, 3308.5s, 3255.1m, 3205.4s, 3160.9m, 2979.5s, 2938.9s, 2877.1m, 2645.8w, 2122.4s, 2079.5s, 1623.2s, 1581.3m, 1549.8s, 1489.8m, 1457.1s, 1383.8m, 1329.2m, 1313.4m, 1282.0m, 1229.9s, 1059.7s, 957.9s, 830.0w, 784.8m, 761.8m, 736.8w, 722.1m, 703.6m, 530.5s, 474.6w, 420.7w cm^{-1}.

$\{[Cd_3(dmatrz)_4(SCN)_6]\}_n$ (5). A mixture of $Cd(NO_3)_2\cdot 6H_2O$ (0.20 mmol), dmatrz (0.40 mmol), NH_4SCN (0.40 mmol), and water (10 mL) was stirred for 5 h and filtered. The filtrate was kept in a $CaCl_2$ desiccator. After a few days, colorless crystals suitable for X-ray analysis were obtained, yield 51%. Anal. Calcd for $C_{22}H_{32}Cd_3N_{22}S_6$: C, 23.52; H, 2.61; N, 27.01. Found: C, 23.28; H, 2.82; N, 27.15. IR (KBr): ν = 3350.0w, 3326.9w, 3208.8m, 2981.5m, 2939.4m, 2877.4w, 2825.2w, 2628.3w, 2109.6s, 2084.2s, 2057.1s, 1989.3w, 1624.7m, 1538.3s, 1457.7m, 1376.5w, 1318.3m, 1278.6w, 1229.3m, 1084.9m, 1048.4s, 973.6m, 912.8s, 791.3m, 758.6m, 711.3m, 517.1w, 491.3w, 469.3m, 424.9w cm^{-1}.

$\{[Cd(dmtrz)(SCN)_2]\}_n$ (6). The synthetic method of complex **6** is similar to that of complex **5** except that the ligand dmatrz was replaced by dmtrz. Colorless crystals suitable for X-ray analysis were obtained in a few days, yield 59%. Anal. Calcd for $C_6H_7CdN_5S_2$: C, 22.05; H, 2.24; N, 21.58. Found: C, 22.11; H, 2.15; N, 21.49. IR (KBr): ν = 3226.5m, 3184.1w, 3153.2m, 3027.2m, 2935.8s, 2839.6s, 2667.6m, 2545.5w, 2497.1w, 2284.8w, 2132.9s, 2101.1s, 2078.1s, 2022.4w, 1709.8w, 1588.1s, 1540.8s, 1493.6w, 1414.6m, 1393.3w, 1373.9m, 1276.8w, 1052.9s, 1011.2w, 945.6w, 866.2s, 748.2m, 724.1s, 670.9m, 616.3w, 467.4m, 445.1w cm^{-1}.

Crystal Structure Determination. Diffraction intensities for the six complexes were collected on a computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation with radiation wavelength 0.71073 Å by using the ω-scan technique. Lorentz polarization and absorption corrections were applied.[44] The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELX-97 and SHELXL-97 programs.[45,46] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[47] The crystallographic data and selected bond lengths and angles for **1**−**6** are listed in Tables 1−7, respectively. CCDC-210634 (**1**), -210631 (**2**), -210635 (**3**), -210632 (**4**), -210630 (**5**), and -210633 (**6**) contain

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

Cd(1)−N(1)	2.243(5)	Cd(1)−N(5)	2.262(5)
Cd(1)−Br(2)	2.5184(14)	Cd(1)−O(1)	2.618(4)
Cd(1)−Br(1)	2.6415(18)	Cd(2)−N(6)	2.250(5)
Cd(2)−N(2)	2.278(5)	Cd(2)−Br(4)	2.5252(14)
Cd(2)−Br(3)	2.6406(18)	Cd(2)−O(1)	2.648(4)
N(1)−N(2)	1.397(6)		
N(1)−Cd(1)−N(5)	113.12(19)	N(1)−Cd(1)−Br(2)	115.41(14)
N(5)−Cd(1)−Br(2)	121.87(15)	N(1)−Cd(1)−O(1)	73.23(16)
N(5)−Cd(1)−O(1)	72.66(16)	Br(2)−Cd(1)−O(1)	92.64(11)
N(1)−Cd(1)−Br(1)	96.97(14)	N(5)−Cd(1)−Br(1)	97.39(14)
Br(2)−Cd(1)−Br(1)	106.38(5)	O(1)−Cd(1)−Br(1)	160.95(10)
N(6)−Cd(2)−N(2)	113.41(19)	N(6)−Cd(2)−Br(4)	115.72(14)
N(2)−Cd(2)−Br(4)	120.97(14)	N(6)−Cd(2)−Br(3)	97.89(14)
N(2)−Cd(2)−Br(3)	95.39(14)	Br(4)−Cd(2)−Br(3)	108.01(5)
N(6)−Cd(2)−O(1)	71.37(17)	N(2)−Cd(2)−O(1)	73.26(16)
Br(4)−Cd(2)−O(1)	93.43(11)	Br(3)−Cd(2)−O(1)	158.56(10)
Cd(1)−O(1)−Cd(2)	92.98(14)	C(1)−N(1)−N(2)	106.5(5)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

Cd(1)−O(1)	2.322(2)	Cd(1)−N(3)	2.324(3)
Cd(1)−Cl(3)	2.5822(12)	Cd(1)−Cl(1)	2.6074(12)
Cd(1)−Cl(3)#1	2.6202(12)	Cd(1)−Cl(2)	2.6577(12)
Cd(2)−N(4)	2.346(3)	Cd(2)−N(4)#2	2.346(3)
Cd(2)−Cl(1)#2	2.6376(12)	Cd(2)−Cl(1)	2.6376(12)
Cd(2)−Cl(2)	2.6558(12)	Cd(2)−Cl(2)#2	2.6558(12)
Cl(3)−Cd(1)#1	2.6202(12)		
O(1)−Cd(1)−N(3)	95.00(9)	N(3)−Cd(1)−Cl(3)	95.69(8)
O(1)−Cd(1)−Cl(3)	82.29(7)	O(1)−Cd(1)−Cl(1)	98.88(7)
N(3)−Cd(1)−Cl(1)	86.37(8)	Cl(3)−Cd(1)−Cl(1)	177.55(3)
N(3)−Cd(1)−Cl(3)#1	173.60(7)	O(1)−Cd(1)−Cl(3)#1	88.56(7)
Cl(3)−Cd(1)−Cl(3)#1	90.05(4)	Cl(1)−Cd(1)−Cl(3)#1	87.83(4)
N(3)−Cd(1)−Cl(2)	86.56(7)	O(1)−Cd(1)−Cl(2)	172.02(7)
Cl(3)−Cd(1)−Cl(2)	89.77(4)	Cl(1)−Cd(1)−Cl(2)	89.02(4)
Cl(3)#1−Cd(1)−Cl(2)	90.65(3)	N(4)−Cd(2)−N(4)#2	180.00(16)
N(4)−Cd(2)−Cl(1)#2	94.95(7)	N(4)#2−Cd(2)−Cl(1)# 2	85.05(7)
N(4)−Cd(2)−Cl(1)	85.05(7)	N(4)#2−Cd(2)−Cl(1)	94.95(7)
Cl(1)#2−Cd(2)−Cl(1)	180.000(14)	N(4)−Cd(2)−Cl(2)	87.14(7)
Cl(1)#2−Cd(2)−Cl(2)	91.57(4)	N(4)#2−Cd(2)−Cl(2)	92.86(7)
Cl(1)−Cd(2)−Cl(2)	88.43(4)	Cl(1)#2−Cd(2)−Cl(2)# 2	88.43(4)
N(4)−Cd(2)−Cl(2)#2	92.86(7)	Cd(1)−Cl(1)−Cd(2)	83.93(4)
N(4)#2−Cd(2)−Cl(2)#2	87.14(7)	Cd(2)−Cl(2)−Cd(1)	82.61(4)
Cl(1)−Cd(2)−Cl(2)#2	91.57(4)	Cd(1)−Cl(3)−Cd(1)#1	89.95(4)
Cl(2)−Cd(2)−Cl(2)#2	180.00(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 2, -y, -z + 1$; #2, $-x + 2, -y, -z$.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **3**[a]

Cd(1)−N(1)	2.344(5)	Cd(1)−N(4)	2.358(5)
Cd(1)−Cl(2)	2.4937(19)	Cd(1)−Cl(1)	2.5760(16)
Cd(2)−N(2)#2	2.6178(16)	Cd(1)−Cl(4)#1	2.9712(18)
Cd(1)−Cl(3)	2.377(5)	Cd(2)−Cl(1)	2.5674(18)
Cd(2)−N(2)	2.377(5)	Cd(2)−Cl(1)#2	2.5674(18)
Cd(2)−Cl(4)#1	2.6747(16)	Cd(2)−Cl(4)#3	2.6747(16)
Cd(3)−N(5)	2.317(5)	Cd(3)−N(5)#1	2.317(5)
Cd(3)−Cl(2)#1	2.5775(16)	Cd(3)−Cl(2)	2.5775(16)
Cd(3)−Cl(4)#1	2.6980(16)	Cd(3)−Cl(4)	2.6980(16)
Cl(4)−Cd(2)#4	2.6747(16)	Cl(4)−Cd(1)#1	2.9712(18)
N(1)−Cd(1)−N(4)	157.85(16)	N(1)−Cd(1)−Cl(3)	102.95(13)
N(4)−Cd(1)−Cl(3)	98.62(13)	N(4)−Cd(1)−Cl(1)	97.63(12)
N(1)−Cd(1)−Cl(1)	84.46(11)	Cl(3)−Cd(1)−Cl(1)	97.72(6)
N(1)−Cd(1)−Cl(2)	87.47(12)	Cl(3)−Cd(1)−Cl(2)	97.68(6)
N(4)−Cd(1)−Cl(2)	84.73(11)	Cl(1)−Cd(1)−Cl(2)	163.87(5)
N(1)−Cd(1)−Cl(4)#1	81.48(12)	N(4)−Cd(1)−Cl(4)#1	76.97(12)
Cl(3)−Cd(1)−Cl(4)#1	175.57(6)	Cl(1)−Cd(1)−Cl(4)#1	82.55(5)
Cl(2)−Cd(1)−Cl(4)#1	82.46(5)	N(2)#2−Cd(2)−N(2)	180.000(1)
N(2)#2−Cd(2)−Cl(1)	92.40(13)	N(2)−Cd(2)−Cl(1)	87.60(13)
N(2)#2−Cd(2)−Cl(1)#2	87.60(13)	N(2)−Cd(2)−Cl(1)#2	92.40(13)
Cl(1)−Cd(2)−Cl(1)#2	180.0	N(2)#2−Cd(2)−Cl(4)#1	97.22(11)
N(2)−Cd(2)−Cl(4)#1	82.78(11)	Cl(1)−Cd(2)−Cl(4)#1	88.89(5)
Cl(1)#2−Cd(2)−Cl(4)#1	91.11(5)	N(2)#2−Cd(2)−Cl(4)#3	82.78(11)
Cl(1)−Cd(2)−Cl(4)#3	91.11(5)	N(2)−Cd(2)−Cl(4)#3	97.22(11)
Cl(4)#1−Cd(2)−Cl(4)#3	180.0	Cl(1)#2−Cd(2)−Cl(4)#3	88.89(5)
N(5)−Cd(3)−N(5)#1	180.000(1)	N(5)#1−Cd(3)−Cl(2)#1	85.46(12)
N(5)−Cd(3)−Cl(2)#1	94.54(12)	N(5)−Cd(3)−Cl(2)	85.46(12)
N(5)#1−Cd(3)−Cl(2)	94.54(12)	Cl(2)#1−Cd(3)−Cl(2)	180.0
N(5)−Cd(3)−Cl(4)#1	83.94(11)	Cl(2)#1−Cd(3)−Cl(4)#1	91.16(4)
N(5)#1−Cd(3)−Cl(4)#1	96.06(11)	Cl(2)−Cd(3)−Cl(4)#1	88.84(4)
N(5)−Cd(3)−Cl(4)	96.06(11)	N(5)#1−Cd(3)−Cl(4)	83.94(11)
Cl(2)#1−Cd(3)−Cl(4)	88.84(4)	Cl(2)−Cd(3)−Cl(4)	91.16(4)
Cl(4)#1−Cd(3)−Cl(4)	180.0	Cd(3)−Cl(2)−Cd(1)	91.59(5)
Cd(2)−Cl(1)−Cd(1)	91.27(5)	Cd(2)#4−Cl(4)−Cd(3)	161.69(7)
Cd(2)#4−Cl(4)−Cd(1)#1	81.09(4)	Cd(3)−Cl(4)−Cd(1)#1	81.98(4)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, -y + 2, -z$; #2, $-x, -y + 2, -z + 1$; #3, $x, y, z + 1$; #4, $x, y, z - 1$.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**[a]

Cd(1)−N(1)#1	2.278(8)	Cd(1)−N(2)	2.371(10)
Cd(1)−N(3)	2.373(7)	Cd(1)−N(7)	2.429(7)
Cd(1)−Cl(1)	2.634(3)	Cd(1)−S(1)	2.739(3)
Cd(2)−N(4)	2.384(7)	Cd(2)−N(4)#2	2.384(7)
Cd(2)−N(8)	2.413(8)	Cd(2)−N(8)#2	2.413(8)
Cd(2)−Cl(1)	2.573(2)	Cd(2)−Cl(1)#2	2.573(2)
N(1)#1−Cd(1)−N(2)	89.5(3)	N(1)#1−Cd(1)−N(3)	94.5(3)
N(2)−Cd(1)−N(3)	92.9(3)	N(2)−Cd(1)−N(7)	176.0(3)
N(1)#1−Cd(1)−N(7)	93.6(3)	N(3)−Cd(1)−N(7)	84.3(2)
N(1)#1−Cd(1)−Cl(1)	177.2(2)	N(2)−Cd(1)−Cl(1)	87.9(2)
N(3)−Cd(1)−Cl(1)	86.80(18)	N(1)#1−Cd(1)−S(1)	93.4(2)
N(7)−Cd(1)−Cl(1)	89.07(17)	N(2)−Cd(1)−S(1)	98.1(2)
N(3)−Cd(1)−S(1)	166.51(18)	N(7)−Cd(1)−S(1)	84.27(18)
N(4)−Cd(2)−N(4)#2	180.0	Cl(1)−Cd(1)−S(1)	85.82(9)
N(4)#2−Cd(2)−N(8)	89.1(2)	N(4)−Cd(2)−N(8)	90.9(2)
N(4)−Cd(2)−N(8)#2	89.1(2)	N(4)#2−Cd(2)−N(8)#2	90.9(2)
N(8)−Cd(2)−N(8)#2	180.000(1)	N(4)−Cd(2)−Cl(1)	88.81(18)
N(4)#2−Cd(2)−Cl(1)	91.19(18)	N(8)−Cd(2)−Cl(1)	89.02(19)
N(8)#2−Cd(2)−Cl(1)	90.98(19)	N(4)−Cd(2)−Cl(1)#2	91.19(18)
N(4)#2−Cd(2)−Cl(1)#2	88.81(18)	N(8)#2−Cd(2)−Cl(1)#2	89.02(19)
N(8)−Cd(2)−Cl(1)#2	90.98(19)	Cd(2)−Cl(1)−Cd(1)	94.41(9)
Cl(1)−Cd(2)−Cl(1)#2	180.0		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, -y + 1, -z + 2$; #2, $-x, -y + 1, -z + 1$.

the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, U.K., fax (+44) 1223-336033, e-mail deposit@ccdc.cam.ac.uk).

Results and Discussion

A view of the molecular structure of **1**, together with its numbering scheme, is depicted in Figure 1a. The structure consists of symmetrical binuclear units in which two Cd(II) ions are bridged by two deatrz ligands and one water molecule. The coordination environments around both Cd(II) ions are distorted trigonal bipyramid, with one bromide anion and a bridged oxygen atom in the axial position (O1−Cd1−Br1 = 160.95(10)°). The remaining three sites are occupied via one bromide anion and two nitrogen atoms of triazoles. There are two crystallographically distinct Cd−O distances (2.618(4) and 2.648(4) Å). The angle of Cd1−O1−Cd2 is 92.98(14)°. This gives rise to a Cd···Cd distance of 3.819 Å. When two triazoles form two bridges between cadmium ions, only a small space is left for the third bridging ligand. This seems to be the main driving force in the formation of the present novel binuclear compounds containing the oxygen atom bridges rather than bromide atom bridges. Engelfriet et al. described somewhat related binuclear compounds $[Co_2(4Phtrz)_5(NCS)_4]\cdot 2.7H_2O$[48] and $[Ni_2(4Ettrz)_4(H_2O)(NCS)_4]\cdot 2.5H_2O$,[49] but in these cases no bridged H_2O molecule was observed. Intermolecular hydro-

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **5**[a]

Cd(1)−N(10)#1	2.298(10)	Cd(1)−N(11)	2.331(16)
Cd(1)−N(5)	2.359(9)	Cd(1)−N(1)	2.363(7)
Cd(1)−S(2)	2.640(10)	Cd(1)−N(9)	2.404(7)
Cd(1)−S(2)	2.681(9)	Cd(2)−N(6)	2.322(7)
Cd(2)−N(6)#2	2.322(7)	Cd(2)−N(9)#2	2.324(6)
Cd(2)−N(9)	2.324(6)	Cd(2)−N(2)	2.369(7)
Cd(2)−N(2)#2	2.369(7)		
N(10)#1−Cd(1)−N(11)	88.4(5)	N(10)#1−Cd(1)−N(5)	85.5(4)
N(11)−Cd(1)−N(5)	170.7(4)	N(11)−Cd(1)−N(1)	90.8(4)
N(10)#1−Cd(1)−N(1)	172.1(3)	N(5)−Cd(1)−N(1)	94.2(3)
N(10)#1−Cd(1)−N(9)	90.1(3)	N(11)−Cd(1)−N(9)	89.0(4)
N(5)−Cd(1)−N(9)	84.0(3)	N(1)−Cd(1)−N(9)	82.0(2)
N(10)#1−Cd(1)−S(2)	96.6(6)	N(11)−Cd(1)−S(2)	80.0(4)
N(1)−Cd(1)−S(2)	91.0(6)	N(5)−Cd(1)−S(2)	107.6(4)
N(10)#1−Cd(1)−S(2)	87.0(3)	N(9)−Cd(1)−S(2)	166.9(5)
N(11)−Cd(1)−S(2)	97.1(9)	N(1)−Cd(1)−S(2)	100.9(3)
N(5)−Cd(1)−S(2)	89.5(9)	N(9)−Cd(1)−S(2)	173.2(9)
S(2)−Cd(1)−S(2)	19.9(4)	N(6)−Cd(2)−N(6)#2	180.000(1)
N(6)−Cd(2)−N(9)#2	93.0(3)	N(6)#2−Cd(2)−N(9)#2	87.0(3)
N(6)−Cd(2)−N(9)	87.0(3)	N(6)#2−Cd(2)−N(9)	93.0(3)
N(9)#2−Cd(2)−N(9)	180.000(1)	N(6)−Cd(2)−N(2)#2	89.6(3)
N(6)#2−Cd(2)−N(2)#2	90.4(3)	N(9)#2−Cd(2)−N(2)#2	86.9(2)
N(9)−Cd(2)−N(2)#2	93.1(2)	N(6)#2−Cd(2)−N(2)	89.6(3)
N(6)−Cd(2)−N(2)	90.4(3)	N(9)#2−Cd(2)−N(2)	93.1(2)
N(9)−Cd(2)−N(2)	86.9(2)	N(2)#2−Cd(2)−N(2)	180.000(1)
Cd(2)−N(9)−Cd(1)	103.3(3)	C(10)−S(2)−Cd(1)	100.0(6)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2, y - 1/2, z$; #2, $-x, -y + 1, -z + 1$; #3, $-x + 1/2, y + 1/2, z$.

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for **6**[a]

Cd(1)−N(3)	2.290(4)	Cd(1)−N(8)	2.340(4)
Cd(1)−N(5)	2.347(3)	Cd(1)−N(2)#1	2.374(4)
Cd(1)−S(2)	2.7354(16)	Cd(2)−N(4)#2	2.280(4)
Cd(1)−S(1)	2.7456(16)	Cd(2)−N(6)	2.353(3)
Cd(2)−N(9)	2.387(3)	Cd(2)−S(4)	2.7208(15)
Cd(2)−S(1)	2.7338(14)	Cd(2)−S(3)#3	2.7717(16)
N(3)−Cd(1)−N(8)	91.31(13)	N(3)−Cd(1)−N(5)	90.89(12)
N(8)−Cd(1)−N(5)	96.27(11)	N(3)−Cd(1)−N(2)#1	90.47(13)
N(8)−Cd(1)−N(2)#1	174.46(11)	N(5)−Cd(1)−N(2)#1	88.94(12)
N(3)−Cd(1)−S(2)	95.03(10)	N(8)−Cd(1)−S(2)	87.98(8)
N(5)−Cd(1)−S(2)	172.63(9)	N(2)#1−Cd(1)−S(2)	86.64(9)
N(3)−Cd(1)−S(1)	172.25(9)	N(8)−Cd(1)−S(1)	86.21(8)
N(5)−Cd(1)−S(1)	82.10(8)	N(2)#1−Cd(1)−S(1)	92.69(9)
S(2)−Cd(1)−S(1)	92.22(5)	N(4)#2−Cd(2)−N(6)	91.37(12)
N(4)#2−Cd(2)−N(9)	91.40(13)	N(6)−Cd(2)−N(9)	92.42(11)
N(4)#2−Cd(2)−S(4)	93.93(10)	N(9)−Cd(2)−S(4)	91.44(8)
N(6)−Cd(2)−S(4)	173.36(9)	N(4)#2−Cd(2)−S(1)	175.77(9)
N(6)−Cd(2)−S(1)	85.86(9)	N(9)−Cd(2)−S(1)	85.52(9)
S(4)−Cd(2)−S(1)	89.06(4)	N(4)#2−Cd(2)−S(3)#3	92.67(11)
N(9)−Cd(2)−S(3)#3	175.24(8)	N(6)−Cd(2)−S(3)#3	85.03(9)
S(4)−Cd(2)−S(3)#3	90.73(5)	S(1)−Cd(2)−S(3)#3	90.28(5)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y, -z$; #2, $-x + 2, -y + 1, -z$; #3, $x, -y + 1/2, z - 1/2$; #4, $x, -y + 1/2, z + 1/2$.

gen bonds, which are expected to play an important role in the stabilization of the structure, exist between the bridging water molecules and terminal bromide anions (O1⋯Br1A = 3.331 Å; O1⋯Br3A = 3.392 Å) and form a 1D chain as shown in Figure 1b. Complex **1** is, to our knowledge, the first synthesized binuclear compound with two bridging triazoles together with one bridging oxygen atom, which may offer a new kind of triazole-bridged structure.

When a chloride atom, a bridged ligand of a smaller size, is used instead of a bromide atom, complex **2** exhibits a zigzag 1D chain. The chain can be considered as constructed by the basic unit, which is composed of linear trinuclear cadmium cations, doubly bridged by μ_2-Cl atoms. The fundamental unit is shown in Figure 2a. In the fundamental unit, neighboring Cd(II) ions of the centrosymmetric trinuclear species are linked by one bridged triazole ligand and two chloride atoms. Four chloride atoms are coordinated to the central cadmium atom and form a square plane, with the octahedron of the central ion compressed along the N4−Cd2−N4A axis, given the distances Cd2−N4 = 2.346(3) Å, Cd2−Cl1 = 2.6376(12) Å, and Cd2−Cl2 = 2.6558(12) Å, respectively. Two chloride anions and one water molecule complete the octahedral coordination sphere of the terminal Cd(II) ions in the unit; the Cd1−Cl distances of 2.582 and 2.620 Å, respectively, are essentially different from the Cd1−N (triazole) and Cd1−Cl distances (Cd1−N3 = 2.324(3) Å, Cd1−Cl1 = 2.6074(12) Å, and Cd1−Cl2 = 2.6577(12) Å). These distances and the ligand−Cd1−ligand angles are indicative of a distorted octahedron around Cd1. The bridging angle Cd1−Cl1−Cd2 = 83.93(4)°. The Cd⋯Cd distance in the trinuclear unit is 3.507 Å. The terminal chloride atoms in the fundamental unit adopt a double bridging mode to connect with other units. On the basis of this connection mode, all trinuclear Cd clusters form a 1D chain along the *a* axis as shown in Figure 2b. Furthermore, the adjacent chains are connected together through hydrogen-bonding interactions, which contain bridged chloride atoms and terminal water molecules with noncoordinated water molecules. Thus, a 2D supramolecular network is formed via both coordinating and hydrogen-bond interaction (Figure 2c). The most striking structure feature of **2** in comparison

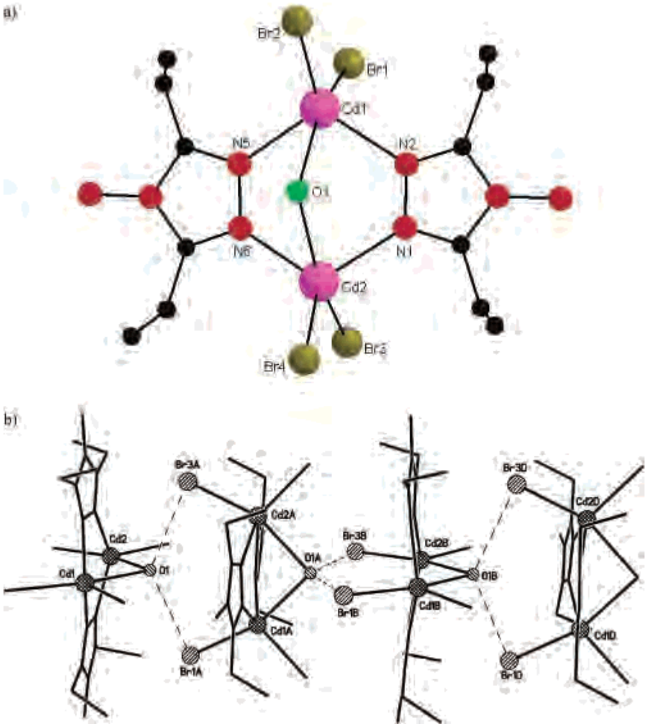

Figure 1. An ORTEP drawing and atomic labeling system showing the structure of **1** (a) and the intermolecular hydrogen-bond interactions of the one-dimensional chain packing in **1** (b). Key: O, green; Cd, purple; N, red; C, black; Br, brown.

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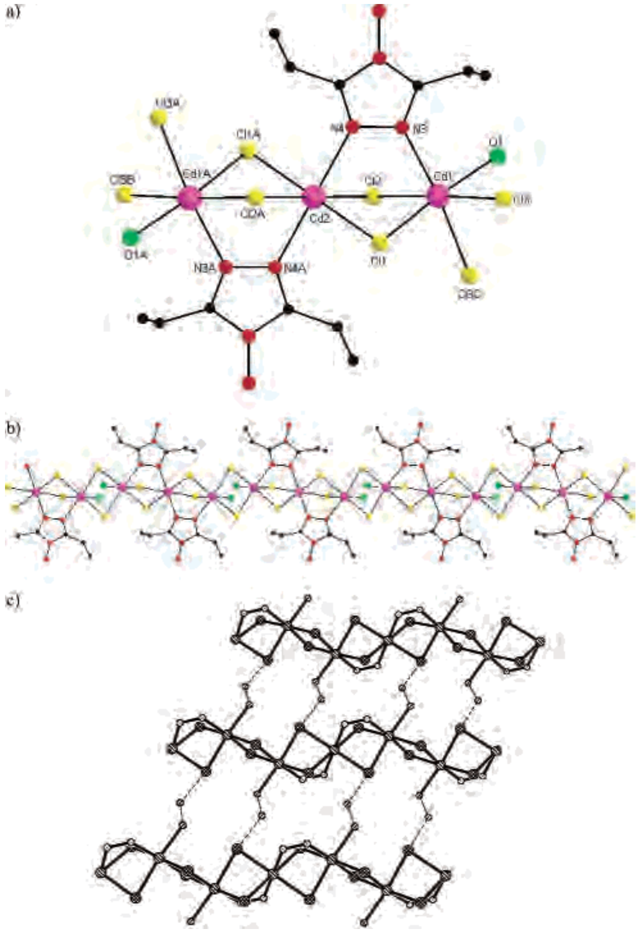

Figure 2. Trinuclear fundamental unit (a), one-dimensional chain structure in **2** (b), and packing diagram with hydrogen bonds (c), omitting noncoordination atoms of triazole rings. Key: N, red; Cl, yellow; Cd, purple; C, black; O, green.

to other 1D triazole−metal complexes[53,57,61−64] is that the chain is the first example constructed via a trinuclear unit. The polymerization of triazole−metal 1D chains is usually through mononuclear[50,51] or binuclear[52] bridging units. Such a structural feature in **2** is unique, presumably due to steric effects of substituents on the 3 and 5 positions of deatrz ligands.[53]

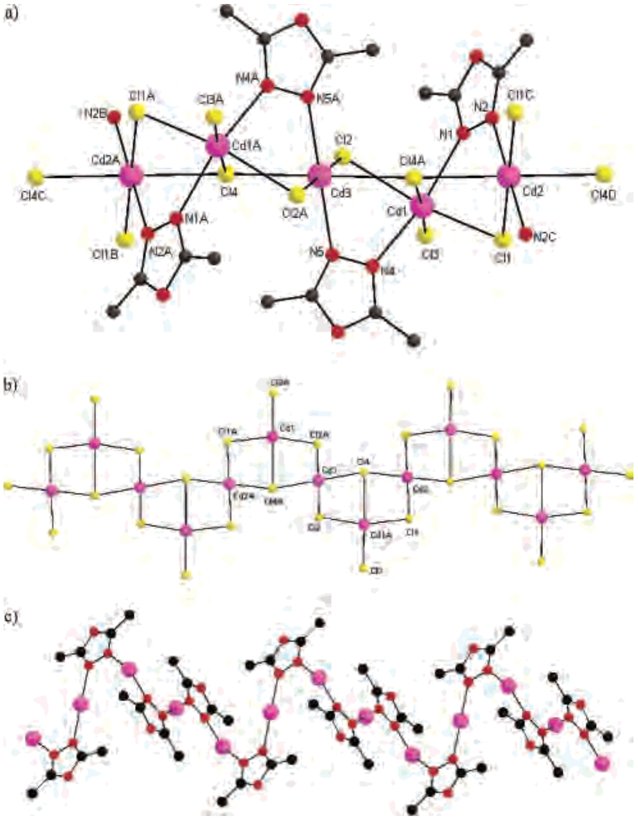

Figure 3. Fundamental unit (a) and one-dimensional structures of cadmium−chloride (b) and cadmium−triazole (c) in **3**. Key: Cl, yellow; Cd, purple; N, red; C, black.

To investigate the influence of the ligand geometry on the assembly of supramolecular structure, dmtrz, which has smaller groups on the 3 and 5 substituents, was used instead of deatrz. Consequently, **3**, which features an unexpected bridging mode, was obtained. In fact, **3** is the first complex containing unprecedented μ_3-Cl bridges in the triazole−metal complexes (Figure 3a). It consists of one-dimensional chains formed by triazole ligands and Cd and Cl atoms, containing μ_2-Cl, μ_3-Cl, terminal chloride, and triazole bridges, and cross-linked by hydrogen bonding to give a 3D supramolecular framework. The centrosymmetric unit of **3** consists of five octahedrally coordinated Cd atoms. Cd1 is coordinated by four chloride atoms (one terminal Cl atom, two μ_2-Cl bridges, and one μ_3-Cl bridge) and two nitrogen atoms of bridging triazole ligands. Four chloride atoms (two μ_2-Cl bridges and two μ_3-Cl bridges) and two nitrogen atoms coordinate around the center atom Cd3. The distances of Cd1···Cd2 and Cd1···Cd3 in **3** are 3.677 and 3.724 Å, respectively, which are slightly longer than the Cd···Cd distance in the trinuclear unit of **2**. The framework structure of **3** is formed by linkage involving units. The Cd2 and Cd3 atoms are connected to each other through chloride bridges, giving rise to infinite one-dimensional chains (Figure 3b), and alternating Cd1 and Cd1A atoms are connected above and below these chains by μ_2-Cl and μ_3-Cl type chloride

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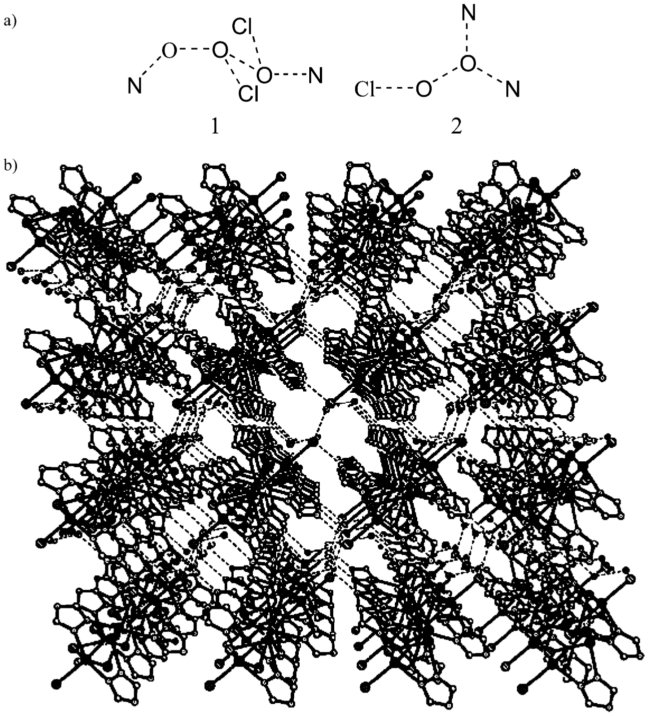

Figure 4. Intermolecular hydrogen bonding (a) and packing of **3** with hydrogen bonds indicated by dashed lines (b).

bridges together with triazole bridges. When all chloride atoms are omitted, each adjacent cadmium atom is bridged by N1,N2-bridged triazoles to form a zigzag chain along the *b* direction (Figure 3c). Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur among the noncoordinated water molecules, the terminal chloride atoms, and the −NH groups of the 3,5-dimethyl-1,2,4-triazole molecules. Therefore, a 3D supramolecular framework is formed as shown in Figure 4. Compared with other bridged triazole complexes,[51,54,55] the most intriguing feature of the structure in **3** is the presence of μ_2-Cl, N1,-N2-triazole together with μ_3-Cl bridges between two metal ions.

When we varied the length of the anions (using SCN$^-$ together with Cl$^-$), **4** was obtained. X-ray crystallographic analysis reveals that **4** is made up of linear trinuclear cadmium units, linked by double SCN$^-$ bridges to form 1D chains. The centrosymmetric trinuclear species is shown in Figure 5a, together with the atomic labeling system used. In the fundamental unit, the central cadmium(II) ion is surrounded by four bridging triazole ligands and two chloride anions. The octahedron of the central Cd(II) ion is compressed along the Cl1−Cd−Cl1A axis, given the distances Cd2−N4 = 2.384(7) Å, Cd2−N8 = 2.413(8) Å, and Cd2−Cl1 = 2.573(2) Å, respectively. Atom Cd2 links to the Cd1 atom via one bridging chloride atom and two N1,N2-bridging 1,2,4-triazole ligands. Two nitrogen atoms and one sulfur atom of different thiocyanate ligands complete the coordination geometry of the distorted octahedral terminal cadmium(II) ion in the unit. The bridging angle Cd2−Cl1−Cd1 is 94.41(9)°, and the Cd1$\cdots$Cd2 distance is 3.821 Å. Only a linear trimer of this bridging type, containing two N1,N2-triazole ligands and a μ_2-Cl atom, has been reported previously.[56] As shown in Figure 5b, the fundamental units are bridged through double μ-1,3-SCN$^-$ bridges to form a zigzag polymer chain along the *a* direction. Two cadmium ions bridged by double μ-1,3-SCN$^-$ ligands form a nearly planar eight-membered ring, Cd(SCN)$_2$Cd, with a Cd$\cdots$Cd separation of 5.829 Å. It is notable that the Cd1$\cdots$Cd2 separation of 3.821 Å doubly bridged by triazole ligands is much shorter than that bridged by thiocyanate ligands in the present compound. It is also noteworthy that though **2** and **4** have the same triazole ligand, they have different fundamental units in the chains. **2** has one bridging triazole ligand and two chloride atoms, while **4** has two bridging triazole ligands and one chloride atom. However, both **2** and **4** have similar 1D zigzag chains which were constructed by trinuclear cadmium cation clusters and linked to each other via double μ_2-Cl for **2** and double μ-1,3-SCN$^-$ for **4**. Bridging modes of N1 and N2 in triazole complexes have been observed before and seem to be a general phenomenon.[38] The most normally bridging modes are three triazoles or triazoles together with anion-bridged metal ions, yielding trinuclear species, especially thiocyanate anions acting as terminal ligands in the trimers.[43,56−61] To the best of our knowledge, no reports on such trinuclear species linked by thiocyanate anions to form polymeric chains have been found.

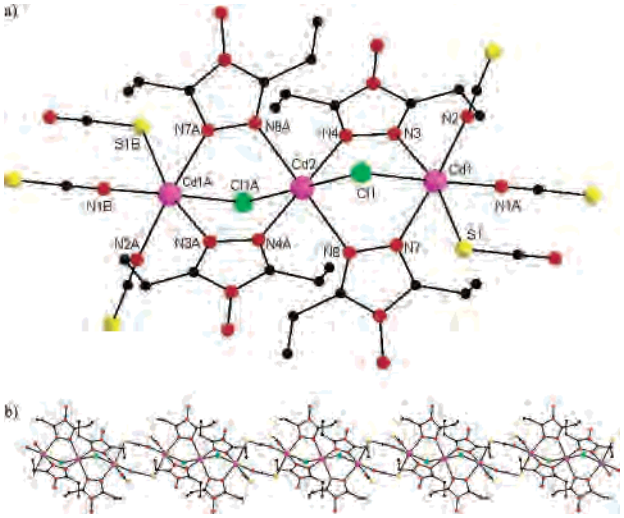

Figure 5. Trinuclear fundamental unit (a) and one-dimensional chain structure (b) in **4**. Key: N, red; Cl, green; C, black; S, yellow; Cd, purple.

To further investigate anion control of thiocyanate ligands, chloride ions were not added and **5** and **6** were obtained. Complex **5** can be considered as constructed from the basic unit, which is composed of trinuclear cadmium cations bridged by two triazole ligands and one thiocyanate, linked via the other thiocyanate ligands to form a 2D polymer in the *ab* plane. The fundamental unit of compound **5** together with the atom labeling is shown in Figure 6a. The S atoms coordinated to Cd ions are disordered with a site occupancy of 50%. In the centrosymmetrical trinuclear units, the central Cd2 ion is located on a crystallographic inversion center, and surrounded by four bridging triazole ligands and two SCN$^-$ anions. The SCN$^-$ ions bridge the terminal cadmium ions only through the nitrogen atom. The terminal cadmium

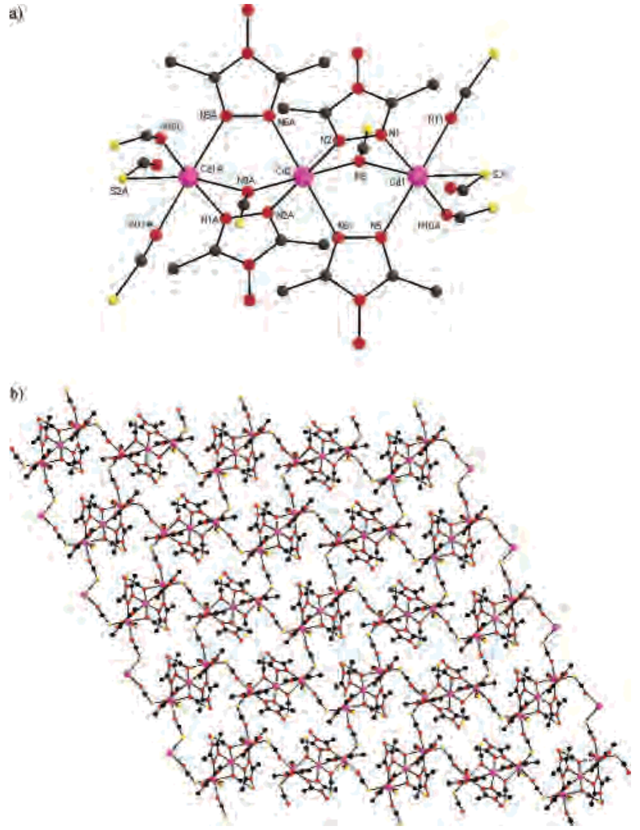

Figure 6. Trinuclear fundamental unit with 50% site occupancy for S2 and S2A (a) and honeycomb-like 2D polymeric network viewed along the *c* direction (b) of **5**. Key: N, red; Cd, purple; S, yellow; C, black.

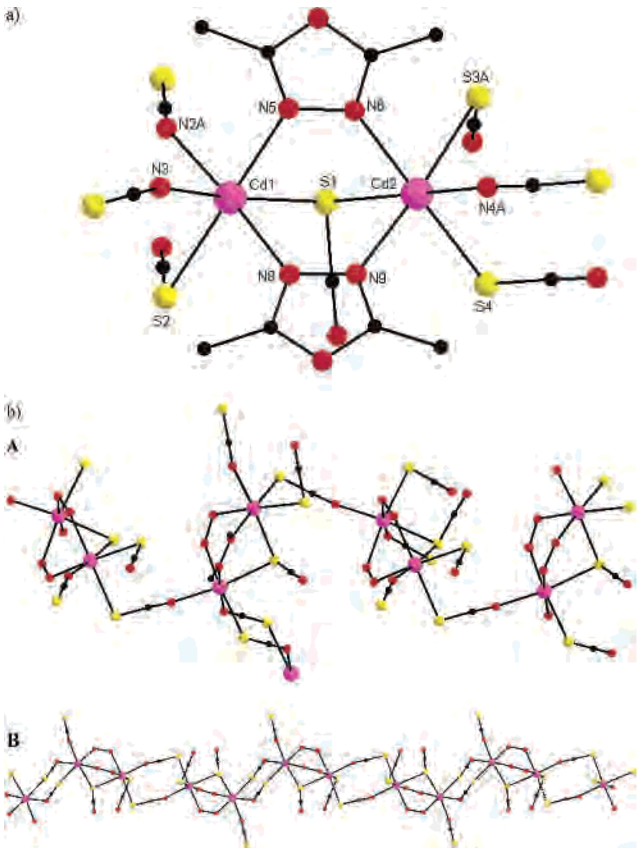

Figure 7. Binuclear unit (a) and two kinds of zigzag chains bridged by thiocyanate groups (b) in **6**. Noncoordination atoms of triazole ligands have been omitted from both chains for clarity. Key: N, red; Cd, purple; S, yellow; C, black.

ions in the unit possess a distorted octahedral geometry. Apart from the three bridging nitrogen atoms (two from triazole and one from SCN^-), three terminal ligands are present (two N atoms and one S atom of different thiocyanate ligands). The C10−S2−Cd1 angle is 100.0(6)°, which is in agreement with the values (100−101.4°) observed in other complexes.[55] The bridging angle Cd1−N9−Cd1 is 103.3(3)°, and the Cd1···Cd2 distance is 3.707 Å. In **5**, each trinuclear unit is connected to four other units through four μ-1,3-SCN^- ligands to result in a 2D honeycomb-like framework along the *c* direction as shown in Figure 6b. It is notable that the Cd1···Cd2 separation is 3.707 Å through double triazole bridges, which is much shorter than those through thiocyanate ligands in **5** (the Cd···Cd distance between adjacent Cd atoms bridged by μ-1,3-SCN^- is 6.397 Å). Three kinds of coordinated modes of SCN^- anions, μ-1,1-bridging $(N)CS^-$, μ-1,3-bridging SCN^-, and terminal SCN^-, were found in the present complex. The μ-1,1-$(N)CS^-$ ligands bridged two cadmium ions to form trinuclear units, and the μ-1,3-SCN^- ligands bridged trinuclear units to form a two-dimensional network structure. The average C−N distance of 1.089 Å and C−S distance of 1.627 Å in these SCN^- moieties show the normal structure of the thiocyanate in the complex. Though we have known a few triazole-bridged trinuclear complexes,[56−61] the 2D structure constructed via these trinuclear units has not been reported. The most interesting feature of this structure is that **5** represents the first case in which the 2D polymer plane is constructed by the bridging triazole−metal trinuclear units.

Unexpectedly, when dmtrz was used instead of dmatrz, structurally different dimensionalities and fundamental units of **6**, under reaction conditions similar to those for the preparation of **5**, were formed. Compared with other reported three-dimensional triazole−metal structures,[63−65] **6** is the first three-dimensional framework based on N1,N2-bridged triazole ligands. The fundamental unit of **6** contains two distinct Cd centers, one μ-1,1-$(S)CN^-$, two triazole-bridged ligands, and six terminal thiocyanate ligands (Figure 7a). In the triazole−metal complexes, bridging of thiocyanate ligands through only the nitrogen atom has been observed before[43,52,58] and seems to be a general phenomenon.[38] However, it is interesting to note that the bridging mode of thiocyanate ligands through the sulfur atom only, on the other hand, is highly unusual and has never been observed. Both Cd1 and Cd2 centers in the asymmetric unit have slightly distorted octahedral coordination geometry. The bond angles around the Cd1 center range from 82.10(8)° to 96.27(11)°, while the bond angles around the Cd2 center range from 85.03(9)° to 93.93(10)°. The Cd1 center coordinates to two nitrogen atoms of the bridged triazole ligands, two nitrogen atoms of μ-1,3-bridged thiocyanate ligands, and two sulfur atoms of SCN^- (μ-1,3- and μ-1,1-bridged) ligands. The Cd2 center binds to three sulfur atoms of SCN^- (two μ-1,3-bridged and one μ-1,1-bridged) groups and three nitrogen

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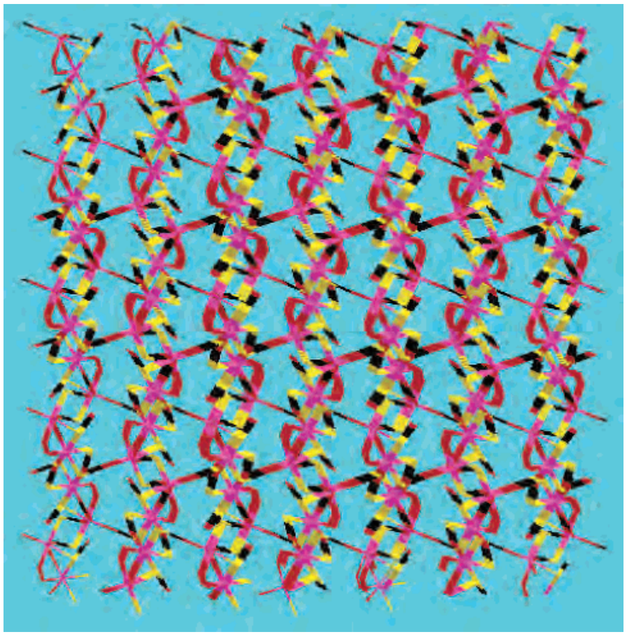


Figure 8. 3D network viewed along the [010] direction in **6**. Noncoordination atoms of triazole ligands have been omitted for clarity. Key: N, red; Cd, purple; S, yellow; C, black.

atoms (two from triazole ligands and one from the thiocyanate ligand) as shown in Figure 7a. The Cd···Cd distance in the binuclear unit is 3.911 Å. Each Cd1 center in **6** is linked to one adjacent Cd2 center via a single μ-1,3-bridged SCN^- group with a Cd···Cd separation of 6.137 Å, and one adjacent Cd1 center by double μ-1,3-SCN^- ligands, forming a nearly planar eight-membered ring, $Cd(SCN)_2Cd$, with a Cd···Cd separation of 5.829 Å. It is noticeable that the Cd1···Cd2 separation of 3.911 Å doubly bridged by triazole ligands is much shorter than that bridged by double thiocyanate ligands, which is also shorter than that bridged by a single thiocyanate ligand. The binuclear units are connected to form two kinds of zigzag chains bridged by a single thiocyanate (chain A) and double thiocyanate groups (chain B) along different directions (Figure 7b). In these chains, thiocyanate ligands act as μ-1,3-bridged ligands. Chain A running in the *a* direction and chain B in the *c* direction cross-link along the crystallographic [010] plane and bridge via SCN^- bridges along the *b* direction to form a 3D network structure (see Figure 8). Viewed from [001] direction, thiocyanate ligands, which only act as double μ-1,3-bridges between metal ions, link the binuclear units to form a 2D framework in the *ab* plane. The topological structure of this plane has two fundamental frameworks, house-like (A) and V-shaped (B), and adopts an ABAB arrangement in the supramolecular network as shown in Figure 9. Two different topological structures exhibit the unique 3D framework of **6**.

Bridging Modes between Metal Ions. The first information worthy of note is that, by controlling synthesis, we obtain six types of bridging modes of 1,2,4-triazoles between two metal ions from the six complexes (Chart 2). The bridging mode N1,N2 is the coordination mode usually found for many triazoles of which the N4-position or 3,5-positions are substituted. In this N1,N2 mode the two metal ions are brought close together at distances of about 4 Å by the first bridging ligand.[38] Because of this, the second and the third ligand, preferably negatively charged, are needed to "ease" the effect of the repulsion of the two metal ions. In the common triple N1,N2-bridging mode, the steric demands of bulky substituents on the 3 and 5 positions may lead the

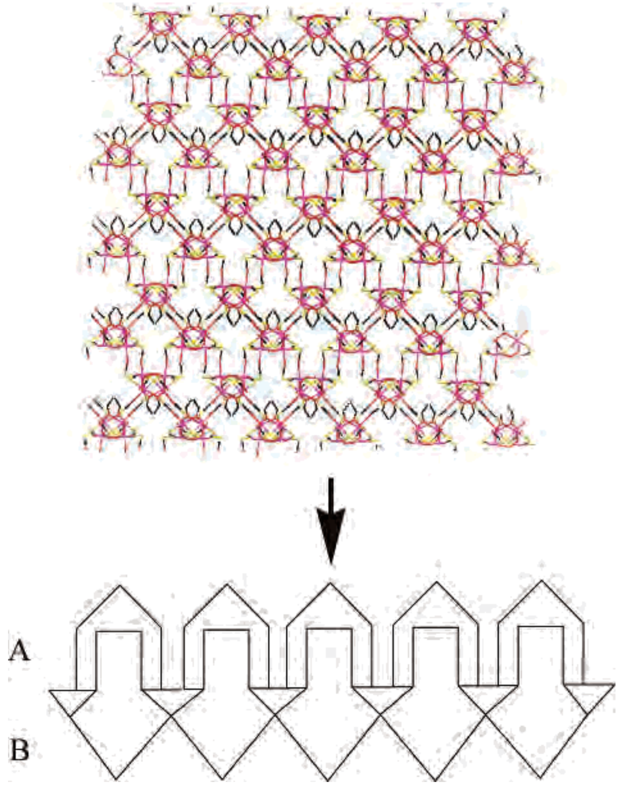
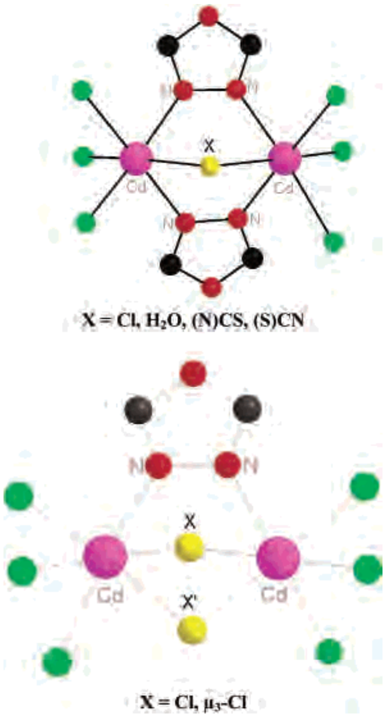


Figure 9. 3D network viewed along the [001] direction in **6**. Noncoordination atoms of triazole ligands have been omitted for clarity. Key: N, red; Cd, purple; S, yellow; C, black.

Chart 2



third ligand to be replaced by small bridging anions or atoms. When bridging anions themselves are bulky, there may only be room for one triazole bridge, in addition to two bridging anions. In the present paper we describe the results of these investigations, using different 3,5-substituted 1,2,4-triazoles with cadmium salts, including crystal structures of all compounds. It has been pointed out again that by using 1,2,4-triazole derivatives, interesting coordination compounds can be obtained. Quite often compounds have been synthesized which show unprecedented structural characteristics. It has been shown now that chelating triazoles with aliphatic side chains also yield novel types of compounds. It is challenging to continue the investigations in this part of the triazole research, because of its interesting bridging and polymeric structural properties.

Coordination Mode of Thiocyanate. Let us now consider the varieties of coordination modes of SCN^- in **4**−**6**. SCN^- is a highly versatile ambident ligand with two donor atoms. It can coordinate through either the nitrogen or the sulfur atom, or both, giving rise to linkage isomers or polymers. The resonance structures are

$$^{-}S{-}C{\equiv}N\ (\mathbf{A}) \leftrightarrow S{=}C{=}N^{-}\ (\mathbf{B}) \leftrightarrow {}^{+}S{\equiv}C{-}N^{2-}(\mathbf{C})$$

The relative importance of the resonance structures follows the trend $\mathbf{A} > \mathbf{B} \gg \mathbf{C}$.[29] The modes of cadmium coordination of thiocyanates are the best understood in terms of the hard−soft acid−base concept developed by Pearson, Basolo, and Burmeister.[66−69] In accordance with the hard−soft acid−base concept, the S atom of the SCN^- ligand, being a soft base, preferentially coordinates to the soft acid whereas the N atom, being a hard base, preferentially coordinates to the hard acid. In the Zn−Cd−Hg triad, the Zn(II) complexes tend to be N-bonded, while the Hg(II) complexes are almost always S-bonded. The Cd(II) ion, in between, becomes “schizophrenic”,[70] exhibiting both (S and N) bonding modes as well as a variety of coordination numbers as we show here. Our findings together with the results concerning SCN^- in **4**−**6** suggest that the thiocyanate ligand has a strong tendency to bridge cadmium(II) ions through its nitrogen and/or sulfur atoms. It is a well-established criterion of infrared spectroscopy that $\upsilon_{as}(NCS) \geq 2100\ cm^{-1}$ indicates a thiocyanate bridge with a 1,3-μ or 1,1,3-μ bridging mode.[11] The strong $\upsilon_{as}(NCS)$ absorption peak at 2122.4 cm^{-1} in complex **4** shows the presence of 1,3-μ-thiocyanate ligands, and that at 2079.5 cm^{-1} is indicative of N-terminal coordination. **5** shows four $\upsilon_{as}(NCS)$ absorption peaks (2109.6 cm^{-1} is assigned to 1,3-μ-SCN^-, 2084.2 and 2057.1 cm^{-1} are assigned to the terminal thiocyanate ligand, and 1989.3 cm^{-1} is assigned to 1,1-μ-bridging (N)CS^-).[43] The infrared spectrum of **6** exhibits two bands in the region near 2000 cm^{-1} (2101.1 and 2078.1 cm^{-1}) which correspond to the $\upsilon_{as}(NCS)$ stretching mode, resulting from a combination of three effects: (1) the presence of single bridging thiocyanate ligands (Cd−SCN−Cd); (2) the presence of double bridging thiocyanate ligands ($Cd(SCN)_2Cd$); (3) the two different distorted octahedral cadmium(II) environments. The absorption peak at 2132.9 cm^{-1} in **6** is assigned to 1,1-μ-bridging (S)CN^-. The FT-IR results are consistent with the crystallographic study.

Table 8. Structural Results of **1**−**6**

complex	anion	organic ligand	bridges in the fundamental units: no. of triazoles	bridges in the fundamental units: atom bridge	structural dimensionality
1	Br^-	deatrz	2	μ_2-Br	zero
2	Cl^-	deatrz	1	μ_2-Cl	one
3	Cl^-	dmtrz	1	μ_2-Cl, μ_3-Cl	one
4	Cl^-/SCN^-	deatrz	2	μ_2-Cl	one
5	SCN^-	dmatrz	2	(N)CS	two
6	SCN^-	dmtrz	2	(S)CN	three

Role of Organic Ligands and Anions in the Construction of Molecular Architecture. The structural results of the six complexes are shown in Table 8. From these results, the choice of anions is clearly critical in determining the molecular architecture of the resultant complex. For example, because of the larger size of the bromide anions in **1**, the polymer chains cannot be formed even if it has the same reaction conditions as **2**. Changing the anion Cl^- to SCN^- has led to the discovery of a new class of two- and three-dimensional structures. **3** has one-dimensional polymer chains, but **5** and **6** form two-dimensional and three-dimensional networks, respectively. The structures of **2** and **4**, which have similar 1D chains, exhibit different N1,N2-triazole bridging modes. This may be due to the longer doubly bridged SCN^- anions instead of Cl^- anions, which may reduce the steric interactions of fundamental trinuclear units. The foregoing facts suggest that a choice of organic ligands would be an ideal way to generate novel polymeric species of cadmium(II). On the basis of this idea, we have chosen three different triazoles. Compared with **2**, **3** is the formation of one-dimensional chains through bridging dinitrogen N−N units rather than halide ions. This may be due to smaller groups on the 3 and 5 substituents of the triazole ligands in **3**. Though **5** and **6** have the same cadmium salt and reaction conditions, because of the amino of dmatrz in **5**, which may obstruct the construction of the 3D network, **5** acts as a 2D plane so as to minimize steric interactions of the organic ligands. Therefore, it can be seen that triazole ligands and anions are playing a controlling role over the network structure. This clearly has wider implications for research in coordination networks.

Conclusion

To provide a facile approach to control the assembly of one-, two-, and three-dimensional extended solids, we have investigated a series of novel triazole−cadmium complexes with a variety of zero-, one-, two-, and three-dimensional frameworks, and novel topologies have been obtained. Subsequent preparation and structural characterization of the

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above complexes have indeed shown that novel types of bridged systems can be obtained through this approach, and this offers the possibility to control the formation of such network structures via varying the organic ligands and anions. This work was also undertaken to obtain more information on the coordination of 1,2,4-triazole ligands. **1** is the first example which uses triazole ligands together with μ-OH_2 as bridges. **2** and **4** are the first polymer chains constructed via the trinuclear metal cation units, which are bridged by triazole ligands. In triazole−metal complexes, the polymer chain of **3** is the first case containing μ_3-Cl bridges. **5** is the first two-dimensional example whose fundamental units are trinuclear metal cations bridged by triazole ligands. **6** is the first three-dimensional example of a N1,N2-didentate coordination triazole−metal compound.

Finally, we stress that previous studies have shown that 1,2,4-triazole ligands and metal ions easily form trinuclear structures, bridged through N1 and N2 atoms. However, to the best of our knowledge, coordination polymers assembled via trinuclear metal cation units, which are bridged by triazole ligands, have not been reported before this work. In this study the present structures of **2**, **4**, and **5** are unprecedented examples of polymer chains and planes constructed via such trinuclear species. On the basis of this work, further synthesis and structural studies of other triazole ligands with cadmium and/or other metals are also under way in our laboratory.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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