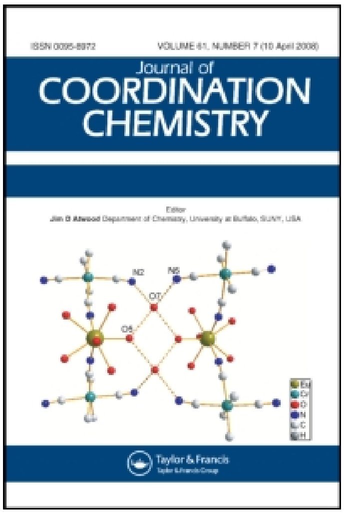

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Synthesis, characterization, and crystal structure of a tricadmium complex of 3,4-diamino-5-methyl-1,2,4-triazole

Mohammad Hakimi[a]; Marcel Maeder[b]; Geoffrey A. Lawrance[b]
[a] Department of Chemistry, Payame Noor University (PNU), Mashhad, Iran [b] Discipline of Chemistry, School of Environmental and Life Sciences, University of Newcastle, Callaghan, NSW 2308, Australia

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Synthesis, characterization, and crystal structure of a tricadmium complex of 3,4-diamino-5-methyl-1,2,4-triazole

MOHAMMAD HAKIMI*†, MARCEL MAEDER‡
and GEOFFREY A. LAWRANCE‡

†Department of Chemistry, Payame Noor University (PNU), Mashhad, Iran
‡Discipline of Chemistry, School of Environmental and Life Sciences,
University of Newcastle, Callaghan, NSW 2308, Australia

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The ligand 3,4-diamino-5-methyl-4H-1,2,4-triazole (DAMT) and its trinuclear cadmium complex [$Cd_3(DAMT)_2(DAMTH)_2Cl_8$] have been prepared and identified by elemental analyses, infrared, Raman, ^1H and ^{13}C NMR spectroscopy, and single crystal X-ray diffraction. The protonation equilibria of the ligand have been studied by pH-potentiometry, with pK_1 13.29 and pK_2 5.40 determined. The free ligand consists of triazole cations (DAMTH) and chloride counter ions. The neutral cadmium compound is a complex of the cationic ligand in which three Cd's are coordinated by two unidentate cation forms of the ligands (DAMTH), two ambidentate neutral forms of the ligand (DAMT), and eight chlorides. Cadmium ions have slightly distorted octahedral geometry.

Keywords: Synthesis; Spectroscopic characterization; X-ray crystal structure; Trinuclear complex; Cadmium(II); Substituted triazole

1. Introduction

Heterocyclic ligands play an important role in the development of coordination chemistry. Amongst five-membered ring systems available, the presence of three nitrogens in triazoles provides an interesting class of compounds. All triazoles are synthetic with no report of detection of this ring system in nature. Nevertheless, 1,2,4-triazole derivatives show diverse pharmacological activities and have been examined as antitumor, antibacterial, antifungal, and antiviral agents [1–4]. Metal complexes containing triazole may also show biological activity [5], providing an impetus for the pursuit of their coordination chemistry.

We have ongoing interest in the coordination chemistry of nitrogen heterocycles. Recently, we studied the behavior of HATT, ATTO, and HAMTT, representative examples of five- and six-membered heterocycles derived from thiocarbohydrazide (1,2,4-triazole and 1,2,4-triazine) with silver(I), copper(I), and cadmium(II) [6–9]. Although 3,4-diamino-5-methyl-4H-1,2,4-triazole (DAMT), examined herein, has been

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*Corresponding author. Emails: hakimi@pnu.ac.ir; mohakimi@yahoo.com

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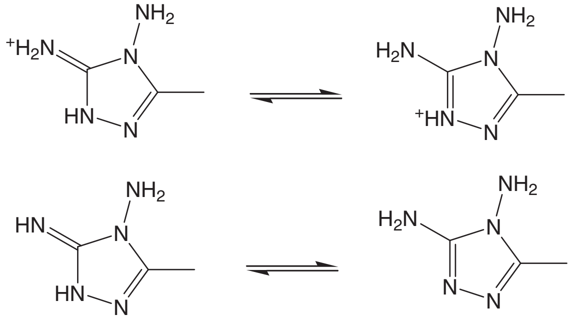

Figure 1. Resonance forms (amine and imine) of the mono-protonated (top) and neutral (bottom) forms of 3,4-diamino-5-methyl-4H-1,2,4-triazole.

reported previously [10], this is the first time that we have managed to crystallize both the ligand and a complex, allowing X-ray crystallographic characterization. DAMTH exists in two resonance forms shown in figure 1, and in the neutral form has tautomers, also shown in figure 1. We report herein how this triazole coordinates either as cationic or as neutral forms to cadmium. Establishment of coordination modes of 1,2,4-triazoles is an important prelude to the wider development of their coordination chemistry and possible applications of their complexes.

2. Experimental

2.1. *Ligand and complex synthesis*

All starting chemicals and solvents were reagent or analytical reagent grade and used as received.

2.1.1. 3,4-Diamino-5-methyl-4H-1,2,4-triazole hydrochloride, DAMT•HCl. The ligand was prepared essentially as described [10] by heating a mixture of 6.25 g (0.05 mol) of 1,3-diaminoguanidine hydrochloride (Aldrich) in 8 mL of glacial acetic acid under reflux for 24 h. On cooling, a white solid separated, which was isolated by dilution with ethanol, further by cooling and filtration. The white crude product was recrystallized from methanol. Colorless single crystals suitable for X-ray analysis were obtained after 24 h. Yield 11.8 g (78%); m.p. 253°C. Anal. Calcd for $C_3H_8ClN_5$ (149.59) (%): C, 24.09 H, 5.39; N, 46.82. Found (%): C, 24.5; H, 5.56; N, 46.7. Infrared (IR) (KBr disc): 3231m (ν_{as} NH_2), 3170 m (ν_s NH_2), 3106 w (ν NH), 2961 w (ν CH), 1682 s (νC=N), 1619 m (δ NH_2), 1393 w (δ_{as} CH_3), 1363 w (δ_s CH_3), 1089 w (ν NN) cm^{-1}. Raman: 3230 w (ν_{as} NH_2), 3165 w (ν_s NH_2), 3103 s (ν NH), 2960 s (ν CH), 1680 m (νC=N), 1620 w (δ NH_2), 1397 w (δ_{as} CH_3), 1362 s (δ_s CH_3), 1091 m (ν NN) cm^{-1}. MS (70 eV): *m*/*z* 14, 16, 18, 19, 29, 44, 57, 69, 83, 112, 113. ^{1}H NMR (d_6-DMSO): δ 2.23 (s, 3H, CH_3); 5.51 (b, 2H, NH_2); 7.57 (b, 3H, NH_2(H)) ppm. ^{13}C NMR (d_6-DMSO): 10.22, 148.94, 165.21 ppm.

2.1.2. Octachloridobis(3,4-diamino-5-methyl-4H-1,2,4-triazole)bis(hydrogen 3,4-diamino-5-methyl-4H-1,2,4-triazole)tricadmium(II) [$Cd_3(DAMT)_2(DAMTH)_2Cl_8$].

A solution of 0.20 g (1.34 mmol) of DAMT · HCl, dissolved in a minimum of EtOH, was added with stirring to a solution of 0.26 g (1 mmol) of $CdCl_2 \cdot 4H_2O$ and NaOAc (0.11 g, 1.34 mmol) in EtOH. The reaction mixture was stirred at 60°C for 1 h. The white crude product produced was collected and washed with cold ethanol. Yield: 0.34 g (94%). To a suspension of complex, 0.34 g in 20 mL ethanol, 1 mL choleric acid in 10 mL ethanol was added at room temperature. Colorless single crystals suitable for X-ray analysis were obtained from the resultant solution after standing for 24 h. Anal. Calcd for $C_6H_{15}Cd_{1.5}Cl_4N_{10}$ (537.68) (%): C, 13.40; H, 2.81; N, 26.05. Found (%): C, 13.26; H, 2.94; N, 25.87. IR (KBr disc): 3220 w (ν_{as} NH_2), 3168 w (ν_s NH_2), 3065 w (ν NH), 2962 w (ν CH), 1664 m (ν C=N), 1623 m (δ NH_2), 1407 w (δ_{as} CH_3), 1364 w (δ_s CH_3), 1073 m (ν NN) cm^{-1}. Raman: 3218 w (ν_{as} NH_2), 3166 w (ν_s NH_2), 3068 w (ν NH), 2963 m (ν CH), 1667 w (ν C=N), 1622 w (δ NH_2), 14010 w (δ_{as} CH_3), 1364 m (δ_s CH_3), 1071 m (ν NN), 331 m (ν CdN), 282, 231 m (ν CdCl) cm^{-1}. ^1H NMR: (d_6-DMSO) δ 2.25 (s, 12H, CH_3); 5.86 (b, 8H, NH_2); 7.81 (b, 10H, $NH_2(H)$) ppm.

2.2. *Physical measurements*

IR spectra were obtained using a Nicolet Model 800 Fourier transform infrared (FTIR) spectrometer, at spectral resolution of 2 cm^{-1}, with 400 scans. Raman spectra were performed using a Nicolet Model 910 Fourier-transform Raman spectrometer. The excitation of the Raman spectrum in the instrument was by the near-IR line at 1.064 µm (or 9398.5 cm^{-1}) from a 3 W cw Nd:YAG laser. About 2000 scans at a resolution of 2 cm^{-1} were needed to ensure high signal-to-noise ratio. ^1H NMR spectra were recorded on a Bruker BRX-500 Avance NMR spectrometer. Chemical shifts are given in parts per million, with values in reference to an internal standard of TMS. The mass spectrum was recorded on a VG 70-S Micromass spectrometer operating at 70 eV. Carbon, hydrogen, and nitrogen analyses were performed in a Heraeus CHN–O rapid elemental analyzer. Protonation equilibria of the ligand were determined by pH-potentiometry, using an autotitrator, temperature-controlled, and stirred glass cell fitted with a pH electrode, all were computer controlled. Analysis of data employed in-house software.

2.3. *X-ray crystallography*

The crystal data and parameters for data collection, structure determination, and refinement are summarized in table 1. Diffraction data for DAMTH were collected on a Rigaku/MSC Mercury CCD diffractometer and calculations were performed using the SHELXL-97 program [11]. Structures were solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and all hydrogens isotropic. Reflection data with $|I| > 2.0\sigma(I)$ were used (table 2).

The diffractometer utilized for data collection of the Cd complex was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas Monochromator (HOG crystal) and Picker X-ray generator are interfaced to a 280 microprocessor, which is controlled by an RS232 serial port on an IBM microcomputer. Motors are Slo-Syn stepping motors and a special top/bottom-left/right slit

Table 1. Crystallographic data for (DAMT)HCl and [$Cd_3Cl_8(DAMT)_2(DAMTH)_2$].

Empirical formula	$C_3H_8ClN_5$	$C_6H_{15}Cd_{1.5}Cl_4N_{10}$
Formula weight	149.59	537.68
Temperature (K)	293(2)	113(2)
Crystal size (mm^3)	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.1
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2₁/n*
Unit cell dimensions (Å, °)		
a	15.5162(18)	9.1536(5)
b	7.1608(7)	9.4113(5)
c	11.7018(13)	19.0294(9)
β	101.1069(17)	101.567(5)
Volume ($Å^3$), *Z*	1275.8(2), 8	1606.04(14), 2
Calculated density ($Mg\,m^{-3}$)	1.558	2.224
F(000)	624	1044
$2\theta_{max}$ (deg)	51.88	52.46
Limiting indices	$-20 \le h \le 20$; $-9 \le k \le 9$; $-14 \le l \le 15$	$-12 \le h \le 10$; $-12 \le k \le 12$; $-25 \le l \le 19$
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)	Mo-Kα ($\lambda = 0.71073$ Å)
Parameters	114	196
Absorption coefficient (mm^{-1})	0.51	2.68
Reflections collected	5541	8161
Unique reflections	1392	3685
R_{int}	0.010	0.058
Goodness-of-fit	1.066	0.974
Reflections with $F_o > 4\sigma(F_o)$	1347	2434
Largest difference peak and hole ($eÅ^{-3}$)	−0.21/0.33	−0.978/1.984
Final R_1[a] (obs. data)	0.0236	0.0580
Final wR_2[b] (all data)	0.0562	0.1306

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0546P)^2$.
[$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 1.6248P]$, where $P = (F_o^2 + 2F_c^2)/3$.
$F_c^* = kF_c[1 + 0.001F_c^2\sigma^3/\sin(2\sigma q)]^{-1/4}$].

Table 2. Experimental interatomic distances (Å) and angles (°) of $DAMTH^+$.

N3–N5	1.4064(12)	C8–N4–N6	104.59(9)
N4–C8	1.3023(14)	C9–N5–C8	107.63(9)
N4–N6	1.3963(13)	C9–N5–N3	121.94(9)
N5–C9	1.3546(14)	C8–N5–N3	130.31(9)
N5–C8	1.3829(13)	C9–N6–N4	111.41(9)
N6–C9	1.3287(15)	N4–C8–N5	110.55(9)
N2 C9	1.3249(15)	N4–C8–C7	126.91(10)
C7–C8	1.4826(14)	N5–C8–C7	122.54(10)
		N2–C9–N6	129.66(10)
		N2–C9–N5	124.53(10)
		N6–C9–N5	105.81(9)

assembly is used to align the crystal. All computations are performed on IBM compatible microcomputer systems using DOS or OS/2 operating systems. Data were collected using a standard moving crystal, moving detector technique with a fixed background at each extreme of the scan. Data were corrected for Lorentz and polarization effects and the equivalent data averaged to yield a unique set of intensities and estimated errors.

The data collections were carried out at 113(2) K. The structure was readily solved by direct methods (MULTAN78) and standard Fourier techniques. All hydrogens were clearly visible in a difference Fourier map phased on the non-hydrogen parameters. In the final full-matrix least squares refinement all positional parameters were varied, as well as isotropic thermal parameters for hydrogens and anisotropic thermal parameters for non-hydrogen atoms. In addition, an overall scale factor and isotropic extinction parameter were varied. Solution and refinement employed SHELXS-97 [12] and SHELXL-97 [11]. Plots are from ORTEP [13] and PLATON-94 [14].

3. Results and discussion

The nitrogen-rich ligand DAMT, with three rings and two pendant nitrogens, can be conveniently synthesized in high yield [10], and thus presents a convenient ligand for a wide range of metal ions. Spectroscopic characterization of the isolated DAMT salt agrees with the reported data [10]. The protonation of the ligand involves addition to the amine on the carbon between two ring nitrogens, with the protonated species able to exist in two resonance forms (amine and imine), as defined in figure 1. A second protonation is possible at the second pendant amine. Determination of two pK_a values in a potentiometric titration is consistent with this. Although two protonation sites are available in DAMT, they differ substantially with potentiometric titrations yielding pK_1 of 13.294(5) and pK_2 of 5.404(3). The pK_a values of 1,2,4-triazoles increase with amine substitution. The parent unsubstituted 1,2,4-triazole has a pK_a of 2.2, changing to 3.72 for 3-amino and to 4.43 for the 3,5-diamino compounds. The value for the 3,4-diamino compound determined here of 5.40 is similar to that for the 3,5-substituted compound, and consistent with the trend. Apart from reporting the pK_a of 3-amino-1,2,4-triazole as 3.72(1) at 25°C in 0.1 mol L^{-1} aq $NaClO_4$, Ercag and coworkers [15] also determined complexation constants with Co(II) and Ni(II), finding logβ_3 of 4.54 (Co) and 6.95 (Ni).

The ligand may bind monodentate or bidentate to a single metal ion, although bridging modes linking two metal ions are also possible. For most metals, monodentate coordination is practicable, and it is anticipated that binding to an imine nitrogen of the ring will be preferred. However, chelation may occur and involve two adjacent ring nitrogens (unlikely, leading to a three-membered chelate ring), one ring and one pendant amine (forming a four-membered ring), or else two pendant N-donors (leading to a five-membered chelate ring). Bridging between two metal ions may permit more facile binding of two adjacent ring N atoms. This latter option is observed herein.

The crystal structure of the monoprotonated free heterocycle (DAMTH, figure 2 and table 1) displays an essentially flat five-membered ring with protonation of the nitrogen in the 2-position (N6). This protonation site is identical to that found in 3-amino-1,2,4-triazole and is also the site of protonation in the unidentate form of the ligand bound to Cd(II) in the trinuclear complex discussed below. Hydrogen-bonding interactions involve all amine hydrogens, with the interaction of hydrogens on N3 with the chloride counter-ion apparent in figure 2. The bond distances and ring sizes of 3-amino-1,2,4-triazole [16] and 3,4-diamino-5-methyl-1,2,4-triazole are similar (figure 3). For example, the sum of bond distances in the former (6.732 Å) and the latter (6.765 Å) are very similar; the very slightly expanded ring in the latter probably results from the higher level of substitution. Relative bond distances C9–N2

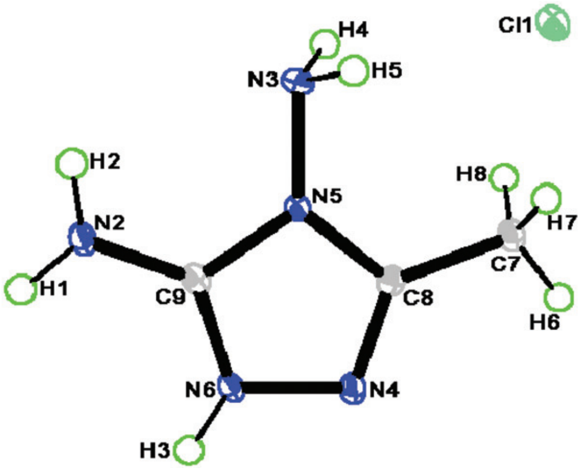

Figure 2. A view of 3,4-diamino-5-methyl-4H-1,2,4-triazole hydrochloride, (DAMTH)Cl.

(exo to the ring, 1.325 Å) and C9–N6 (in the ring, 1.329 Å) are both greater than the C8–N4 double bond, not involved in such a resonance process (1.302 Å) and do not heavily favor the resonance form with the imine in the ring (figure 1) and protonated. However, the ring nitrogen is where the proton is located in the structure. Notably, in the bridged coordination mode where both 1- and 2-ring nitrogens are bound to cadmium and unable to participate in protonation and associated resonance behavior, the N1–C1 distance (1.312 Å) and the N5–C2 distance (1.307 Å) are very similar and distinctly shorter than the exo C1–N2 distance (1.375 Å).

Vibrational spectra of the ligand salt and the cadmium complex show a complex set of bands associated with the amine and imine functionalities. The IR spectra of $[Cd_3(DAMT)_2(DAMTH)_2Cl_8]$ shows absorption bands at 3065 (IR) and 3068 cm^{-1} (Raman), which can be assigned to ν NH; the asymmetric and symmetric NH_2 stretching bands of the complex shift to lower frequencies. The labile complex species in solution is not the "frozen" protonated form seen in the solid state and discussed below, and only an averaged NMR spectrum is seen, as expected.

The cadmium trimer (figure 4) displays a center of symmetry about the central cadmium. The central Cd1 is coordinated in a distorted octahedral shape by four bridging chlorides that occupy the one approximate plane with Cd1 and two axial nitrogens (N1) that correspond to the nitrogen that is protonated in free ligand (N6 in figure 2). Each terminal Cd2 is bound by two bridging and two terminal chlorides in the central plane, with two different nitrogen donors in axial sites. One is the adjacent nitrogen (N5) of a ligand to that binding to the central Cd1; the other is the same type of nitrogen (N6) of another ligand that is protonated at the adjacent nitrogen (N7) and hence binds monodentate, although there is a close hydrogen-bond interaction between the H on N(7) and Cl4 on Cd2. The bidentate bridging ligand displays bond distances (table 3) that are significantly shorter (1.50–2.10 Å) than those of the monodentate nitrogen donor, perhaps associated with the closer approach producing a better fit, as angles subtended at Cd are not significantly distorted. Further, the protonation of the monodentate amine may promote a longer Cd–N distance. Terminal chlorides display

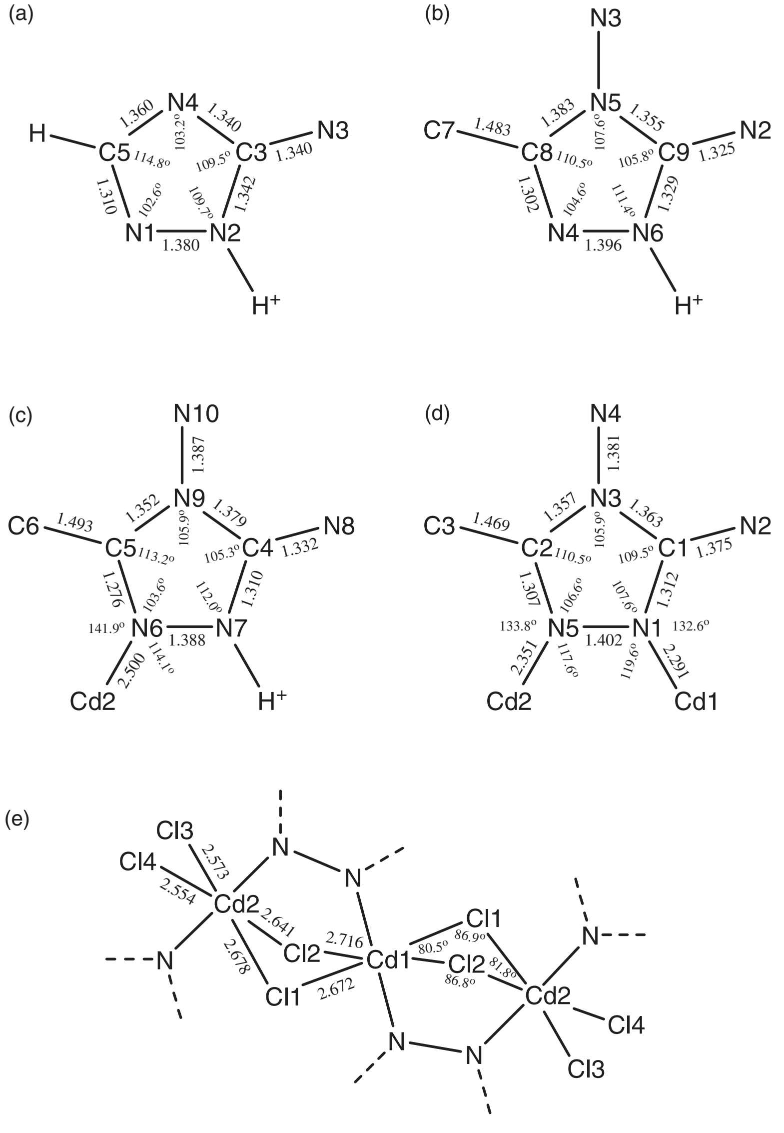

Figure 3. Bond distances and angles in the protonated forms of (a) 3-amino-1,2,4-triazole (literature data), (b) 3,4-diamino-5-methyl-1,2,4-triazole, (c) 3,4-diamino-5-methyl-1,2,4-triazole bound to one cadmium(II) ion, and also (d) 3,4-diamino-5-methyl-1,2,4-triazole bound as a neutral ligand to two cadmium(II) ions. The common site of protonation in the first three is defined by the H^+. Coordination around the tricadmium(II) unit is illustrated in (e), highlighting bonding distances and angles involving chloride. Numbering schemes are those used in other figures and tables.

Cd–Cl distances that are ~1.00 Å shorter than those of bridging chlorides, with the terminal Cl3–Cd2–Cl4 the angle is opened out from the ideal by ~7°, whereas for the bridging Cl1–Cd2–Cl2, the angle is compressed by about the same amount (figure 3(e)). Each Cd displays a *trans*-$CdCl_4N_2$ donor set, and the sum of metal–donor distances for the core Cd1 (15.359 Å) and the terminal Cd2 (15.297 Å) are comparable.

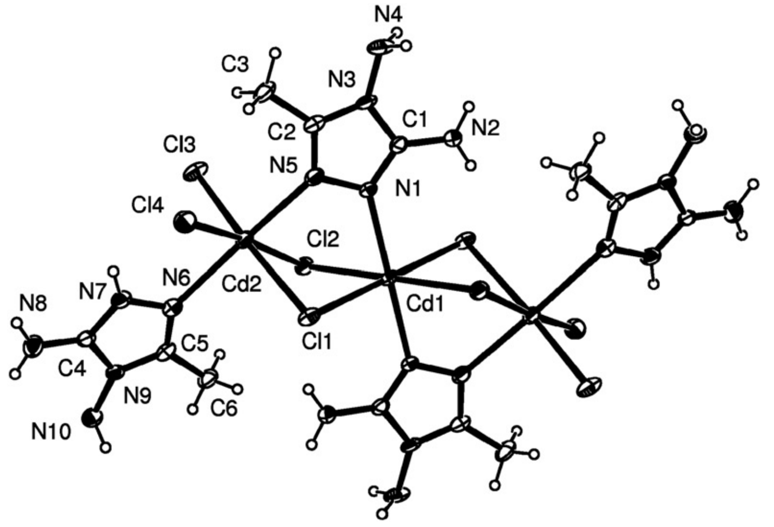

Figure 4. A view of the trinuclear cluster [$Cd_3(DAMT)_2(DAMTH)_2Cl_8$].

Table 3. Distances (Å) and angles (°) subtended about cadmium in [$Cd_3Cl_8(DAMT)_2(DAMTH)_2$].

	Cd2	N6	N5	Cl4	Cl3	Cl2
Cl1	2.6783(18)	93.51(15)	84.12(15)	92.93(7)	170.31(7)	81.78(6)
Cl2	2.6407(19)	92.88(16)	88.88(16)	174.27(6)	88.55(6)	
Cl3	2.5728(19)	87.62(15)	95.07(15)	96.76(7)		
Cl4	2.554(2)	85.22(16)	92.78(16)			
N5	2.351(6)	176.8(2)				
N6	2.500(7)					
	Cd1	N1′	N1	Cl2′	Cl2	Cl1′
Cl1	2.672(2)	88.81(17)	91.19(17)	99.48(6)	80.52(6)	180.0
Cl1′	2.672(2)	91.19(17)	88.81(17)	80.52(6)	99.48(6)	
Cl2	2.7164(18)	84.49(15)	95.51(15)	180.000(1)		
Cl2′	2.7164(18)	95.51(15)	84.49(15)			
N1	2.291(6)	180.000(2)				
N1′	2.291(6)					

The coordination observed in this trimer resembles somewhat that found in the bridging Zn_2L_2 unit in [$Zn_4L_4(SCN)_4$]$\cdot H_2O$, where L is the closely related ligand 3-amino-1,2,4-triazole [17]. In that case, the approximately tetrahedral Zn ions are linked by two bridging triazoles in the same fashion as found here, with an additional monodentate triazole and a thiocyanate ligand. Notably, in neither case are pendant amines employed in coordination, with ring nitrogens employed exclusively.

4. Conclusion

The 1,2,4-triazole ligand containing one pendant methyl and two pendant nitrogens and its tricadmium complex have been characterized by physico-chemical and spectroscopic methods. The spectral and X-ray studies show that the ligand is a unipositive monodentate *via* N6 or neutral bridging group *via* N1 and N5, in either way coordinating to the cadmiums. The crystal structure of the free ligand indicates that hydrogen bonds and N2–H2 ··· Cl1 interactions cause 3-D supramolecular expansion of the compound. The N8–H8 ··· Cl3 and N7–H7 ··· Cl3 interactions in the *bc* plane give a supramolecular network in the complex. Comparison with similar complexes having different substituents on the coordinated triazole ring clearly shows that the substituent on the triazole ring has considerable effect on the structure of such complexes. We are now trying to achieve high-quality single crystals of other metal complexes of this ligand in order to obtain their structural data for comparison with the complex.

Supplementary material

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-742946 for (DAMT)HCl and CCDC-748470 for the Cd(II) complex $[Cd_3(DAMT)_2(DAMTH)_2Cl_8]$. Copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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