Monomer, Dimer, Tetramer, Polymer: Structural Diversity in Zinc and Cadmium Complexes of Chelate-Tethered Nucleobases

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Abstract: A series of Zn^{II} and Cd^{II} complexes of adenine and guanine derivatives containing a diamine tether have been isolated from aqueous solutions and characterised by single crystal X-ray analysis. These studies reveal a wide range of structural types including monomeric, dimeric, tetrameric and polymeric architectures. The extended structures arise from the ability of the ligands to bridge metal ions using the chelating tether in conjunction with N7 of the nucleobase. Additional metal–nucleobase co-ordination is generally observed at the N3-site of the adenine derivatives. With Cd^{II}, ethylenediamine-N9-ethylguanine forms an inverted G-tetrad type structure.

Keywords: G-quartet · hydrogen bonds · nucleobases · metal binding · nanostructures

Introduction

Coordinate bond formation is increasingly used to assemble extended structures either as discrete geometric entities, such as helicates, triangles, squares and hexagons, or as polymeric structures.[1–4] Nucleobases, because of their propensity for binding metal ions through a variety of bonding modes, including bridging interactions, are well suited for generating such multi-component molecular architectures.[5–8] These systems have even been shown to be capable of including guest molecules.[7] Furthermore, the capacity of nucleobases to form inter-molecular hydrogen bonds provides an additional directional interaction which may be exploited for molecular aggregation with the formation of extended hydrogen bonded arrays.[6, 7]

Towards this we have recently begun to investigate the co-ordination chemistry of a series of chelate-tethered nucleobase derivatives.[8] We have previously described monomeric and polymeric complexes, including a cationic polynucleotide analogue, derived from these ligand systems.[8c] In this work we report on Zn^{II} and Cd^{II} complexes of ethylenediamine-tethered derivatives of adenine and guanine. X-ray crystallographic characterisation of the products isolated from aqueous solutions reveals a diversity of structural types including mono-, di-, tetra- and polymeric species. The results demonstrate the application of chelate-tethered nucleobases in generating extended molecular structures based on metal–ligand bond formation.

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Results and Discussion

Zn^{II} complexation: Crystals isolated from an aqueous solution containing a 1:1 stoichiometric mixture of $Zn(ClO_4)_2$ and A-Et-enH·Cl (A-Et-enH·Cl: ethylenediamine-N9-ethyladenine hydrochloride) were characterised as $[Zn(Cl)(A\text{-}Et\text{-}en))(H_2O)][ClO_4]$ **1**, by single crystal X-ray analysis. The metal ion adopts a distorted trigonal bipyramidal co-ordination geometry (∢N12-Zn-O1 166.5°; sum of equatorial angles = 360°) as shown in Figure 1. The A-Et-en acts as a tridentate ligand and binds the metal ion via the diamine function and N3 of the adenine moiety. This binding mode is analogous to that seen in Cu^{II} complexes containing adenine-diamine derivatives though in these cases the metal ion adopts a square pyramidal geometry.[8a, c] The remaining co-ordination sites are occupied by a water molecule and a chloride anion. The adenine moiety lies at an angle of 115° with respect to the plane defined by Zn1/N3/Cl1/N15.

By contrast, crystals isolated from aqueous solution of $ZnCl_2$ and A-Et-enH·Cl, again present in 1:1 stoichiometry, contain $[(Zn_3Cl_6(A\text{-}Et\text{-}en)_2(H_2O)_2]$ **2**, a centrosymmetric molecule with a metal:nucleobase ratio of 3:2, see Figure 2. The trinuclear molecular unit contains two unique Zn ions.

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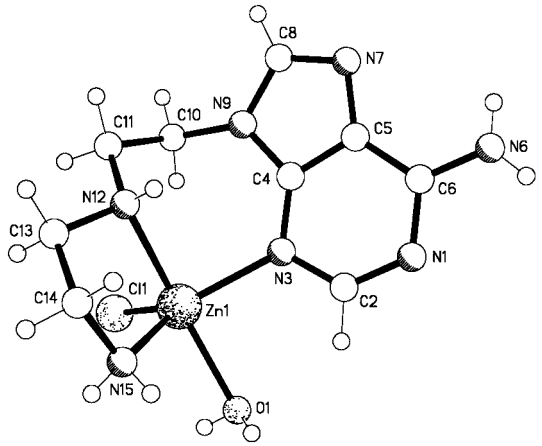

Figure 1. Molecular structure of the monomeric **1**. Selected bond lengths [Å]: Zn1–N3 2.0701(16), Zn–N12 2.1807(19), Zn–N15 2.071(2), Zn–O1W 2.1787(17), Zn–Cl1 2.2465(6).

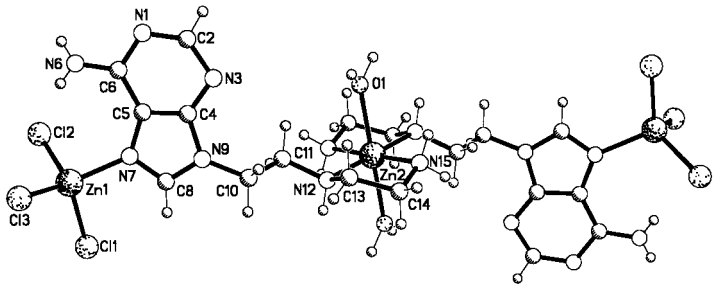

Figure 2. Molecular structure of the trimetallic complex in **2**. Selected bond lengths [Å]: Zn1–N7 2.004(8), Zn1–Cl1 2.268(5), Zn1–Cl2 2.271(4), Zn1–Cl3 2.257(5), Zn1A–N7 1.973(18), Zn1A–Cl1A 2.248(15), Zn1A–Cl2A 2.244(13), Zn1A–Cl3A 2.254(14), Zn2–N13 2.137(7), Zn2–N16 2.121(8), Zn2–O1 2.261(7).

The octahedral Zn2 ion is co-ordinated by two diamine functions and a *trans*-arrangement of H_2O molecules. The pendant adenine moieties each co-ordinate at N7 to a $[ZnCl_3]^-$ group.

A search of the Cambridge Crystallographic Data Base found several examples of zinc complexes containing adenine or guanine derivatives. Interestingly, these predominantly feature coordinated $[ZnCl_3]^-$ groups at the N7 position. The Zn–N7 bond length ranges from 2.077 to 2.094 Å from five structures.[9] The values in **2** are similar.

Some aspects of the structural differences observed in the solid state are supported by results obtained from analyses in solution. For example, titrations of A-Et-enH·Cl with $Zn(ClO_4)_2$ carried out in D_2O and followed by ^1H NMR spectroscopy show a loss of fine-structure for resonances corresponding to the $-CH_2CH_2-$ chains (Figure 3). In addition, slight shifts, when compared with those of the free ligand, are also seen. For example, the protons on C10 and C11 (using the labels of the X-ray structures) move downfield slightly, from $\delta = 4.10$ to 4.25 and $\delta = 2.92$ to 3.04, respectively. The aromatic protons are also slightly shifted, H8 from $\delta = 7.87$ to 7.98 and H2 from $\delta = 7.88$ to 8.06. The most dramatic difference, however, is the broadening of one of the aromatic proton resonances of the nucleobase, which is observed as the metal ion concentration increases. The linewidth of the H8 resonance is constant over the entire metal:ligand concentration ranges at 2.1 Hz; by contrast the H2 resonance increased to 30 Hz at equimolar metal:ligand ratio. On the basis of ROESY experiments this proton can be confirmed as H2 and the broadening of this signal is consistent with metal ion interacting at an adjacent site, that is N3.[10] However, this effect was seen to be anion dependent. For example, $Zn(NO_3)_2$ gave similar results to those obtained for $Zn(ClO_4)_2$ (H2 = 34 Hz and H8 = 2 Hz for 1:1 Zn:ligand concentration); in contrast, $ZnCl_2$ showed negligible effect (H2 = 8, H8 = 2 Hz at 1:1 Zn:ligand ratio). These observations, in agreement with crystal structure evidence, suggest that in the presence of strongly coordinating ligands, such as Cl^- ions, metal–nucleobase interactions may be inhibited or modified leading to the formation of other product(s).

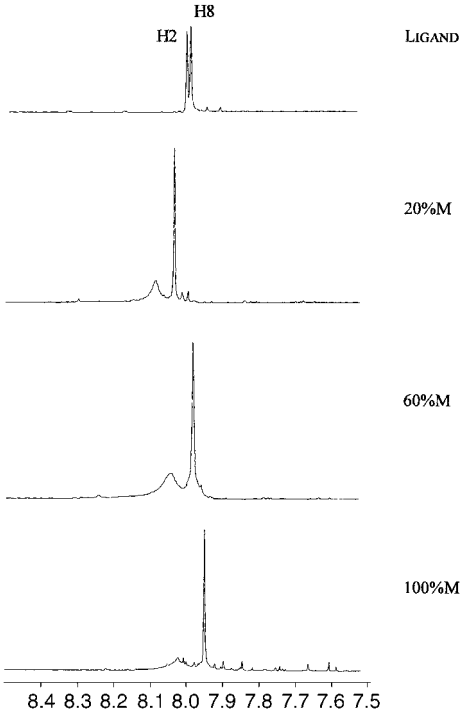

Figure 3. Aromatic region of the ^1H NMR spectrum for $Zn(ClO_4)_2$ and A-Et-enH·Cl in D_2O illustrating the broadening of the H2 resonance of the adenine moiety.

Analysis of solutions using ES-MS also indicated speciation to be highly dependent on the nature of the metal salt used. For example, with $Zn(ClO_4)$, the positive ion ESMS exhibits a major peak at *m*/*z* 222 corresponding to $[A\text{-Et-enH}]^+$. Peaks attributable to complexation are observed which correspond to $[Zn(ClO_4)L]^+$ (*m*/*z* 386) and $[Zn(Cl)L]^+$ (*m*/*z* 322). The negative ion spectrum is dominated by ClO_4^- (*m*/*z* 99), though weak peaks can be assigned for $[Zn(ClO_4)_3L]^-$ (*m*/*z* 584), $LH_2[(ClO_4)_3]^-$ (*m*/*z* 420) and $[Zn(ClO_4)_3]^-$ (*m*/*z* 363).

For solutions containing $ZnCl_2$ and A-Et-enH·Cl (1:1 ratio) positive ion ES-MS revealed the presence of polynuclear species with peaks assigned for the following complexed species: $[Zn_3L_2Cl_5]^+$ (*m*/*z* 815), $[Zn_3L_2Cl_3]^+$ (*m*/*z* 679), $[ZnCl_2LH]^+$ (*m*/*z* 358) $[ZnClL]^+$ (*m*/*z* 322). Interestingly the negative ion ES-MS was dominated by a peak at *m*/*z* 171 corresponding to $[ZnCl_3]^-$. On the basis of these assignments the solid state structure of **2** is perhaps unsurprising.

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The formation of polynuclear species was also observed with the guanine-diamine. ES-MS analysis of aqueous solutions containing G-Pr-enH·Cl and an equimolar equivalent of $Zn(NO_3)_2$ in addition to the peak at *m*/*z* 252 corresponding to $[G\text{-}Pr\text{-}enH]^+$, contained peaks at *m*/*z* 350 and 378 corresponding to $[ZnCl(L)]^+$ and $[Zn(NO_3)L]^+$, respectively. However, crystals isolated from such solutions were shown to contain a dimeric complex, $[\{ZnCl(G\text{-}Pr\text{-}en)\}_2][NO_3]_2$ **3**, Figure 4. In this case the Zn ion adopts a distorted tetrahedral

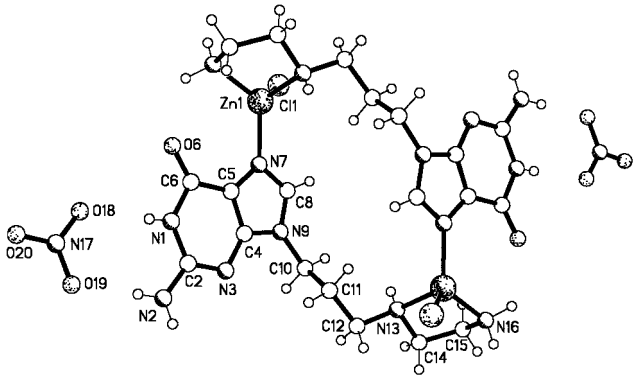

Figure 4. Molecular structure of centrosymmetric dimer **3**. Selected bond lengths [Å]: Zn1–Cl1 2.2321(7), Zn1–N7 2.0021(19), Zn1–N13 2.079(2), Zn1-N16 2.005(2); intramolecular Zn···Zn separation 8.2 Å.

co-ordination geometry, the diamine function, Cl^- and N7 of the guanine moiety are involved in metal ion binding. The molecular unit is centrosymmetric with each diamine function co-ordinating to one metal ion whilst the tethered guanine binds to the second metal ion via N7. There is no interaction with the N3 site. Within the molecule the guanine residues do not stack above one another. Nitrate anions hydrogen bond to the N1 and N2 sites (N1···O18 2.852; N2···N19 2.947 Å) while the O6 site of guanine interacts with an occluded water molecule (O6···O2w 2.901 Å). There is also a relatively short C8-H···O-NO_2^- interaction (C8···O20 3.128 Å), highlighting the polar nature of this C–H bond, which results in chains throughout the crystal lattice.

In fact, the molecular packing in each of the complexes **1**–**3** is stabilized predominantly by hydrogen bonding. Of most interest is a comparison of the base pairs formed in **1** and **2** due to the self-complementary nature of the adenine moieties (Figures 5 and 6). In both cases hydrogen bonded pairs are formed through an interaction of the Watson–Crick faces of the adenine moieties. In **1** the N1···N6A distance is 2.940 Å while in **2** this separation is 2.969 Å. Hence despite the change in the site of metal ion binding in these structures (N3 versus N7) no difference in the hydrogen bonding is observed.

Complexation of Cd^{II}: ^1H NMR spectra of a D_2O solution of $Cd(NO_3)_2$ and A-Et-enH·Cl (1:1 molar ratio) showed significant broadening for the adenine proton H2 in an analogous manner to that observed for $Zn(NO_3)_2$. In fact the magnitude of the broadening was comparable (H2 = 28 Hz and H8 = 3 Hz). Similarly, a loss of fine-structure of the resonances attributed to the methylene chains was observed and again slight differences in the chemical shifts were apparent

Figure 5. The centrosymmetric base-pairing interaction involving the Watson–Crick face of N3-coordinated adenine in **1**. The N1···N6 distance is 2.940 Å.

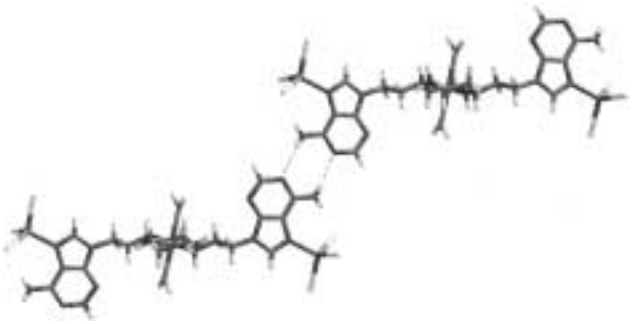

Figure 6. The centrosymmetric base-pairing interaction involving the Watson–Crick face of N7-coordinated adenine in **2**. The N1···N6 distance is 2.969 Å.

compared to the free ligand. The shifts were generally downfield, for example protons on C10 and C11 shifting $\delta =$ 2.92 to 3.05 and $\delta = 4.10$ to 4.25 and also the adenine protons H2 $\delta = 7.88$ to 8.12 and H8 $\delta = 7.87$ to 8.03. ^{113}Cd NMR data for these solutions exhibited two resonances ($\delta = 181$ and 156 in a ratio of 1:10). Comparison with literature data suggests the minor species to involve octahedral co-ordination with oxygen donors.[11] The major species ($\delta = 156$) is indicative of predominantly N-donor ligands.[12]

ES-MS further highlighted the presence of multiple, and also multinuclear, species in solution. In the positive ion spectra peaks at *m*/*z* 370 and 397, which correspond to complexed species $[CdClL]^+$ and $[Cd(NO_3)L]^+$, were observed in addition to less intense peaks at higher molecular weight assigned to polynuclear species: *m*/*z* 773 $[Cd_2Cl_3L_2]^+$, 852 $[Cd_2(NO_3)_3L_2]^+$, and 870 $[Cd_2Cl_2(NO_3)L_2]^+$.

X-ray analysis of crystals isolated from such solutions were characterised as $[\{Cd_2Cl_6(A\text{-}Et\text{-}en)_2\}_n]$ **4**. The isolation of **4** from solutions containing $Cd(NO_3)_2$ and A-Et-enH·Cl in a 1:1 molar ratio is unexpected; however, the tendency for Cd^{II} ions to form halide bridges is well documented and clearly is a significant factor in this case.[13] The structure contains two unique Cd ions; Cd1 occupies a centre of symmetry and is coordinated in an octahedral geometry by four bridging chloride anions, the remaining co-ordination sites being occupied by N7 of adenine moieties. Cd2 is also octahedral though this is rather distorted from idealized geometry. The ligands coordinated to Cd2 comprise three Cl^- anions (two

bridging and one terminal) and three nitrogen donor atoms, provided by the diamine function and N3 of adenine (Figure 7). Hence the same tridentate binding mode is observed as

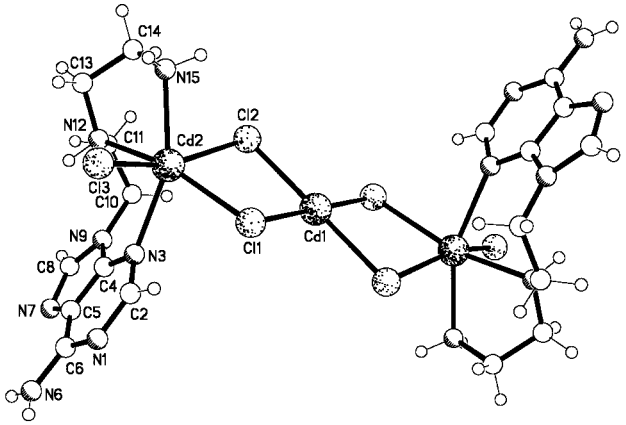

Figure 7. Trimetallic unit in **4**. Selected bond lengths [Å]: Cd1–N7A 2.389(5), Cd1–Cl1 2.6674(19), Cd1–Cl2 2.6097(16), Cd2–N12 2.368(6), Cd2–N15 2.329(6), Cd2–N3 2.418(5), Cd2–Cl1 2.6490(18), Cd2–Cl2 2.7662(18), Cd2–Cl3 2.7132(18); Cd···Cd separations 3.943 Å.

seen in **1**, though in **4** an additional interaction to the ligand at N7 is observed. This resulting combination of bridging interactions generates a polymeric structure that may be considered as an interlocking of trimetallic sheets, the Cd···Cd separation within a sheet being 3.943 Å (see Figure 8).

Figure 8. Polymeric chain in **4** generated by interlocking the trimetallic units through lattice translations along the *b*-axis. The adenine···adenine pairs are slipped with respect to one another and do not exhibit stacking interactions. The Cd···Cd distance along the polymer chain is 8.031 Å.

Pairs of adenine moieties then separate these sheets (intersheet spacing = 8.031 Å as measured for the shortest Cd···Cd distance); however, these bases are not substantially stacked.

To the best of our knowledge there are few cases of structurally characterised Cd-complexes of the purine nucleobases. A search of the Cambridge Crystallographic Data Base found two examples containing adenine; in one case adenine acts to form dimers by bridging two metal centres through co-ordination at N9 and N3.[14a] The other structure contains a chloro bridged *catena* with N7 co-ordinated 9-methyladenine and $(CH_3)_2S{=}O$ acting as additional ligands (Cd–N7 distance 2.358 Å).[14b] A single example of a Cd-containing guanine derivative was found, that of 5′guanosine-monophosphate co-ordinating at N7 to $[Cd(H_2O)_5]^{2+}$ (Cd–N7 distance 2.373 Å).[14c]

Reaction between Cd^{II} ions and a guanine-diamine were investigated with $CdSO_4$ and G-Et-enH·Cl. Aqueous solutions containing an equimolar ratio of these reagents were again shown by ^{113}Cd NMR and ES-MS to contain multiple species. As for A-Et-en, two resonances were observed in the ^{113}Cd NMR spectra ($\delta = 183$ and 119 in a 5:1 ratio). Again one of the resonances ($\delta = 183$) is indicative of a predominantly oxygen-based co-ordination sphere while the less intense resonance is tentatively assigned as involving both N- and O-donors.[11, 12] In the positive ion ES-MS peaks at *m*/*z* 238 for $[G\text{-Et-enH}]^+$ and 385 corresponding to $[CdClL]^+$ were observed along with additional peaks containing Cd-isotopes at *m*/*z* 683 and 795. These could be assigned to $[CdL_2HSO_4]^+$ and to a dimeric species $[Cd_2(L)(L\text{-H})SO_4]^+$, respectively.

X-ray analysis of crystals isolated from aqueous solutions containing these reagents, $[Cd_4G\text{-Et-en})_4(H_2O)_4(SO_4)_4]$ **5**, reveal the same ligand binding mode as observed in the zinc complex, **3**. However, in **5**, a tetrameric assembly is formed in contrast to a dimer. The four octahedral Cd^{II} centres (two unique) lie in a same plane (deviation from the calculated least squares plane is ±0.059 Å) and form the corners of a square. Each is coordinated by a diamine function and N7 of an adjacent guanine moiety, the remaining sites are occupied by H_2O and sulfate anions bonded above and below the tetramer plane as shown in Figure 9. An intramolecular hydrogen bonding interaction is observed within the square involving O6···N15A (2.07 Å).

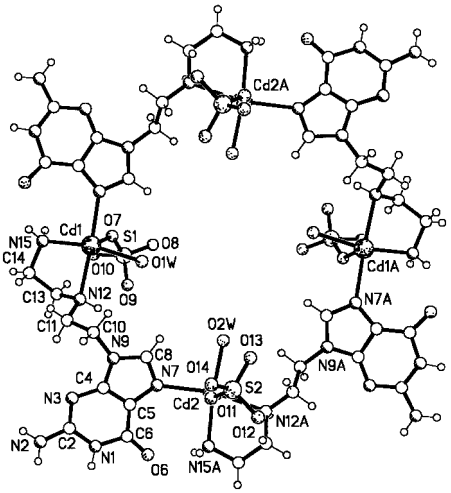

Figure 9. Unique atom numbering scheme for **5**. Selected bond lengths [Å]: Cd1–N12 2.413(19), Cd1–N15 2.291(19), Cd1–N7A 2.308(13), Cd1–O10 2.27(3), Cd1–O1w 2.291(18), Cd1–O7 2.47(2), Cd2–N12A 2.389(13), Cd2–N15A 2.258(14), Cd2–O2w 2.281(13), Cd2–O11 2.452(12), Cd2–O14 2.308(13).

The dimensions of the square are $Cd1\cdots Cd2_{edge}$ 8.729 Å, $Cd1\cdots Cd2A_{edge}$ 7.970 Å and $Cd1\cdots Cd1A_{diagonal}$ 11.451 Å, $Cd2\cdots Cd2A_{diagonal}$ 12.176 Å; corner angles are ∢Cd2-Cd1-Cd2A 86.5° and ∢Cd1A-Cd2-Cd1 93.5°. The extremities of the molecular assembly are defined by the guanine residues, the mean diagonal distance between the exocyclic amino groups being ≈22 Å. Each of the guanine molecules lies at an

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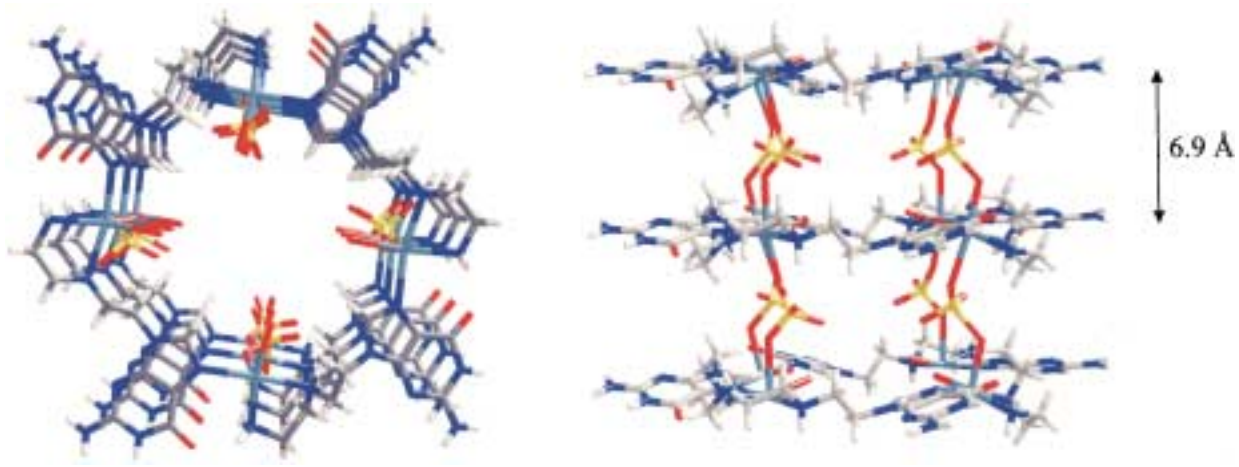

Figure 10. a) Left, view down the C_2 (approximate S_4) axis of a Cd_4–G_4 tetrad column in **5**. The average metal···metal distances are Cd···Cd_{edge} 8.35 and Cd···$Cd_{diagonal}$ = 11.81 Å. b) Right, edge-on view of the G-tetrad column generated by sulfate bridging individual Cd_4–G_4 squares. The interior cavity is occupied with co-ordinated and unco-ordinated water molecules.

angle of either 17.2° or 16.0° to the plane defined by the four cadmium centres. As has been pointed out by Lippert,[5] metal-derived molecular boxes generally form the necessary 90° angles through the *cis*-orientation of metal ion co-ordination sites. By contrast, nucleobases can form 90° angles through (N1+N7) bridging modes. It is noteworthy that in **5** it is the ligands which also form the corners of the box, but here N7 and the diamine are responsible.

Four SO_4^{2-} anions co-ordinated to one face of a square act to bridge metal centres (Cd···Cd distance 6.915 Å) in adjacent squares and in this way a cylindrical polymer is generated (Figure 10). The interior of this assembly is occupied by the co-ordinated water molecules. Inter-cylinder interactions are seen with stacking interactions involving the six-membered rings of the guanine moieties (the inter-base distance is approximately 3.5 Å, each guanine residue is tilted at an angle of 2.5° with respect to its neighbour below) (Figure 11).

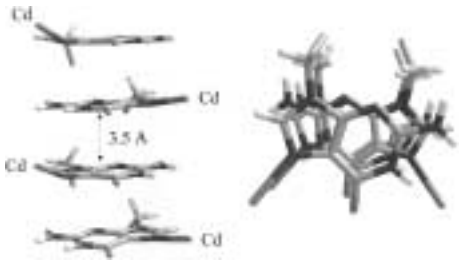

Figure 11. Stacking of G-residues in **5** formed by interactions between neighbouring columns. The stacking distance is ≈3.5 Å.

It is interesting to compare the structure of **5** with other nucleobase-tetramers. The best established is the G-tetrad seen in telomeres (Figure 12).[15] Nucleobase-quartets have also been reported for isoguanine[16] and the guanosine derivative (*N*,*N*-dimethylaniline)guanosine[17] as well as for thymine[18] and uracil.[19]

Superficially there are a number of structural similarities between, for example, the nucleotide quartets formed in telomeres and the Cd_4-G_4 squares in **5**. In both cases the tetramer assembly shows a high degree of planarity and each interacts further to form columnar aggregates. The substantial difference, however, is in the nature of the association. In **5** the tetramer units are assembled through metal–ligand bond formation and the columnar arrangement is a result of sulfate anions bridging adjacent cadmium centres (Figure 10b). The formation of guanine quartets in telomeres on the other hand is based on hydrogen bonding interactions to form individual tetrads and aromatic stacking combined with metal ion binding (e.g. K^+) to form the extended structure. The differing mode of interaction involved in the formation of the two tetrameric assemblies accounts for the "inverted" nature of Cd_4-G_4 square in **5**, as compared to the G-tetrad; in the case of the former the guanine residues point out of the square with their hydrogen bonding faces exposed.

There have been previous reports of molecular squares derived from metallo-nucleobases with both pyrimidine and purine examples represented.[6] In particular cases the complexes have been shown to be capable of further reactivity by co-ordinating metal ions and also to associate neutral guest species in a manner reminiscent to calix[4]arenes.[7]

A unique aspect of **5** as compared to these synthetic, and natural tetrad cases is that because the guanine residues are oriented in an *exo*-arrangement, the ability for Watson–Crick base-pairing interactions is retained. The potential for binding of multiple complementary nucleotides offers an additional means for molecular aggregation. Interestingly, the recent report on the stabilizing effect of Pt^{II} coordination to guanine-N7 of the Watson–Crick G–C base pair[20] suggests that structures based on **5** may form quite stable assemblies with complementary partners under the appropriate conditions (Figure 12).

Summary

Despite the apparent diversity of structural types reported here and elsewhere,[8] some general trends in the binding modes of the chelate-tethered nucleobases are evident.

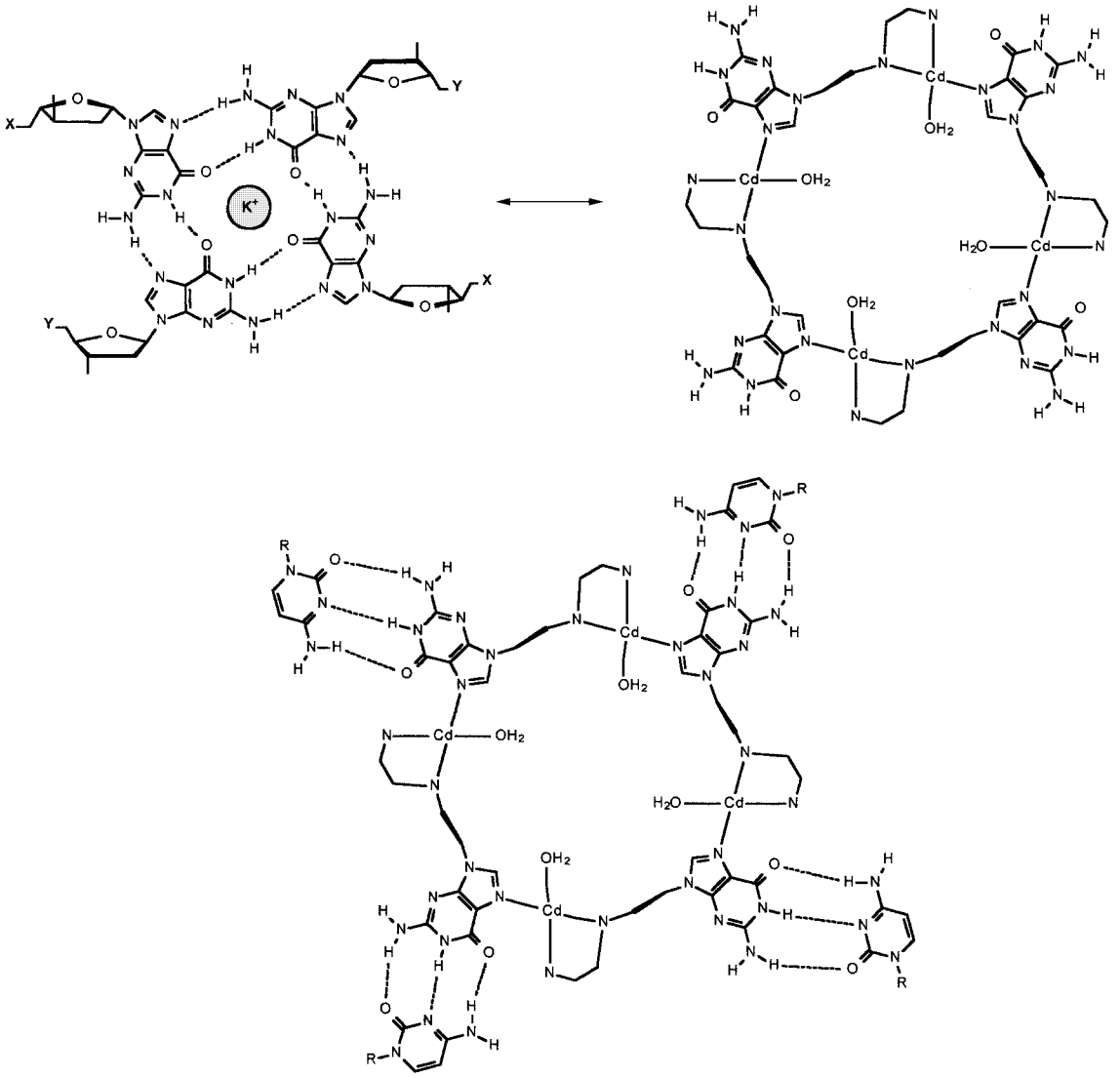

Figure 12. Schematic comparing a G-tetrad (left) with a Cd_4–G_4 square (right) from **5**. Lower centre: an illustration of base pairing of **B** with four cytosine molecules.

Without exception, and irrespective of the nucleobase, the diamine function is seen to chelate to a single metal centre. For the adenine derivatives there is a tendency for tridentate co-ordination involving the minor groove site N3 in conjunction with the diamine. Compound **2** described here is the exception to this. In addition, the adenine moiety may also bind a second metal ion through N7 to form a bridging [3 + 1]-binding mode and thereby generate extended structures. Thus far these have all been polymeric rather than discrete molecular complexes. The chelate binding mode involving the nucleobase is analogous to the *macrochelation* observed for nucleotide phosphates as described by Sigel.[21] In the cases of guanine, to date, N7 binding is observed and hence polynuclear species generally have been isolated.[22] A further point is that the tridentate binding mode involving N3 of the nucleobase is not generally observed.[23] The greater reactivity of the N7 site in guanine as compared to adenine may account for the fewer examples of monomeric complexes containing guanine. The implications of these data are currently being investigated.

Experimental Section

The starting materials $Zn(NO_3)_2 \cdot 6H_2O$, and $Zn(ClO_4)_2$ and the deuterated solvent D_2O were purchased from Aldrich Chemicals. $ZnCl_2$ was purchased from Fluka and the cadmium salts $3CdSO_4 \cdot 8H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ from BDH Chemicals. ^1H, ^{13}C and ^{113}Cd NMR spectra were recorded on a Joel Lambda 500 instrument at 500.13, 125.74 and 177.46 MHz, respectively. ^{113}Cd NMR was also measured on a Bruker AC 300 spectrometer at 66.55 MHz. ^{113}Cd NMR data are referenced to $Cd(ClO_4)_2$ and samples were measured in water. Electrospray mass spectra (ES-MS) were measured at the National Mass Spectrometry Service Centre in Swansea on equimolar aqueous solutions containing metal salts and the appropriate diamine. Elemental analyses were performed using a Carlo Erba 1106 instrument.

Ligand synthesis: The ligands, ethylenediamine-N9-ethyladenine and ethylenediamine-N9-ethylguanine, as hydrochloride salts were prepared as previously reported.[8a, c] Ethylenediamine-N9-propylguanine hydrochloride was prepared in an analogous manner to that described for ethyl derivative employing 1-bromo-3-chloropropane as alkylating agent. ^1H NMR (500 MHz, [D$_6$]DMSO): $\delta = 1.86$ (m, 2H, CH_2-CH_2-CH_2), 2.46 (t, 2H, NH-CH_2-CH_2-CH_2), 2.70 (t, 2H, NH_2-CH_2-CH_2-NH), 2.80 (t, 2H, NH_2-CH_2-CH_2-NH), 4.02 (t, 2H, CH_2-CH_2-Gua), 6.66 (s, 2H, Gua-N2H_2), 7.71 (s, 1H, C8-*H*); ^{13}C NMR (500 MHz, [D$_6$]DMSO): $\delta = 29.39$ (CH_2-CH_2-CH_2), 38.67 (NH_2-CH_2-CH_2-NH), 40.58 (CH_2-CH_2-Gua), 45.32 (NH-CH_2-

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CH_2-CH_2), 46.33 (NH_2-CH_2-*CH_2*-NH), 116.58 (C5), 137.66 (C8), 151.20 (C4), 153.70 (C2), 156.91 (C6); anal. calcd for $C_{10}H_{18}ClN_7O$: C 41.74, H 6.30, N 34.07; found: C 41.17, H 6.47, N 33.25.

Metal complexes 1–5: In each case the metal salt, typically 0.2 mmol, was dissolved in water (1 mL) and to this an equimolar aqueous solution of the appropriate ligand was added with stirring. The solutions were allowed to stand at room temperature from which crystals suitable for single crystal X-ray analysis were obtained. **1**: anal. calcd for $C_9H_{17}Cl_2N_7O_5Zn$: C 24.59, H 3.90, N 22.31; found: C 24.26, H 3.70, N 21.96; **2**: anal. calcd for $C_{18}H_{42}Cl_6N_{14}O_6Zn_3$: C 22.53, H 4.41, N 20.44; found: C 22.15, H 4.38, N 20.44; **3**: anal. calcd for $C_{20}H_{46}Cl_2N_{16}O_{14}Zn_2$: C 25.65, H 4.95, N 23.93; found: C 26.01, H 4.27, N 23.83; **4**: anal. calcd for $C_{18}H_{30}Cd_3Cl_{5.8}N_{14}(NO_3)_{0.2}$: C 21.65, H 3.03, N 19.93; found: C 20.16, H 2.82, N 19.20; **5**: elemental analysis indicated contamination by $CdSO_4$ of the bulk sample isolated from solution. Analysis corresponds to $[Cd_4(C_9H_{15}N_7O)_4(SO_4)_4]\cdot(H_2O)_{13}\cdot(CdSO_4)_2$; calcd C 17.76, H 3.56, N 16.11; found: C 17.53, H 3.54, N 15.81.

X-ray structure analyses: Crystal data for **1**: $[C_9H_{17}ClN_7OZn][ClO_4]$, $M_r = 439.57$, triclinic, space group $P\bar{1}$, $a = 9.0267(13)$, $b = 9.6930(14)$, $c = 11.3338(17)$ Å, $\alpha = 111.318(4)$, $\beta = 98.983(4)$, $\gamma = 108.858(3)^\circ$, $V = 831.0(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.757$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 1.836$ mm^{-1}, $T = 160$ K. Of 5880 measured reflections, corrected for absorption, 4102 were unique ($R_{int} = 0.0240$, $\theta \leq 25.0^\circ$); $R = 0.0389$ (F values, $F^2 > 2\sigma$), $R_w = 0.1082$ (F^2 values, all data), GOF = 1.048 for 238 parameters, final difference map extremes +1.04 and −0.79 e Å^3. The structure was solved by direct methods.

Crystal data for **2**: $[C_{18}H_{42}Cl_6N_{14}O_6Zn_3]$, $M_r = 959.47$, triclinic, space group $P\bar{1}$, $a = 7.0057(8)$, $b = 11.1106(13)$, $c = 12.1936(14)$ Å, $\alpha = 103.111(3)$, $\beta = 90.814(3)$, $\gamma = 93.017(3)^\circ$, $V = 922.76(18)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.727$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 2.422$ mm^{-1}, $T = 160$ K. Of 4732 measured reflections, corrected for absorption, 3156 were unique ($R_{int} = 0.0430$, $\theta \leq 25.0^\circ$); $R = 0.0849$ (F values, $F^2 > 2\sigma$), $R_w = 0.2041$ (F^2 values, all data), GOF = 1.176 for 296 parameters, final difference map extremes +0.93 and −0.87 e Å^3. The structure was solved by direct methods. The terminal $ZnCl_3$ unit is disordered over two sets of positions in the ratio 78.6:21.4(11)%. H-atoms were located and coordinates freely refined for O1 and O1w (both 100% occupied). There is additionally a cavity filled with diffuse and disordered electron density attributed to water of crystallization. This was modeled approximately as one molecule of water split over four positions.

Crystal data for **3**: $[C_{20}H_{46}Cl_2N_{16}O_{14}Zn_2]$, $M_r = 936.37$, triclinic, space group $P\bar{1}$, $a = 7.9014(9)$, $b = 10.3484(11)$, $c = 11.7040(13)$ Å, $\alpha = 93.092(3)$, $\beta = 101.603(2)$, $\gamma = 96.547(3)^\circ$, $V = 928.42(18)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.675$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 1.519$ mm^{-1}, $T = 160$ K. Of 8199 measured reflections, corrected for absorption, 4312 were unique ($R_{int} = 0.0240$, $\theta \leq 28.7^\circ$); $R = 0.0387$ (F values, $F^2 > 2\sigma$), $R_w = 0.0831$ (F^2 values, all data), GOF = 0.990 for 280 parameters, final difference map extremes +0.44 and −0.46 e Å^3. The structure was solved by direct methods.

Crystal data for **4**: $[C_{18}H_{30}Cd_3Cl_6N_{14}]$, $M_r = 992.46$, triclinic, space group $P\bar{1}$, $a = 8.0089(14)$, $b = 9.6202(17)$, $c = 10.1605(18)$ Å, $\alpha = 91.972(5)$, $\beta = 98.622(5)$, $\gamma = 100.696(4)^\circ$, $V = 759.0(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.171$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 2.649$ mm^{-1}, $T = 160$ K. Of 6384 measured reflections, corrected for absorption, 3642 were unique ($R_{int} = 0.0406$, $\theta \leq 29.1^\circ$); $R = 0.0535$ (F values, $F^2 > 2\sigma$), $R_w = 0.1368$ (F^2 values, all data), GOF = 0.954 for 187 parameters, final difference map extremes +2.45 and −1.18 e Å^3. The structure was solved by direct methods. All H-atoms are in geometric positions. There is approx. 10% NO_3^- at the site of Cl3, but this could not be successfully modeled; it accounts for the main residual electron density

Crystal data for **5**: $[C_{36}H_{78}Cd_4N_{28}O_{31}S_4]$, $M_r = 1977.10$, orthorhombic, space group $P2_12_12$, $a = 22.726(4)$, $b = 22.771$ (4), $c = 6.9147(11)$ Å, $V = 3578.3(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.835$ g cm^{-3}; synchrotron radiation, $\lambda = 0.6942$ Å, $\mu = 1.390$ mm^{-1}, $T = 160$ K. Of 11636 measured reflections, corrected for absorption, 4856 were unique ($R_{int} = 0.0524$, $\theta \leq 22.5^\circ$); $R = 0.1100$ (F values, $F^2 > 2\sigma$), $R_w = 0.2661$ (F^2 values, all data), GOF = 1.128 for 480 parameters, final difference map extremes +3.50 and −3.06 e Å^3 with the largest features close to Cd. The structure was solved by direct methods from synchrotron data because of the very weak diffraction from poor quality crystals. There is some minor twinning of the structure to emulate tetragonal symmetry and also racemic twinning.

Programs used: SHELXTL (G. M. Sheldrick, SHELXTL manual, Bruker AXS Inc., Madison, WI, USA, **1998**, version 5.1), SQUEEZE procedure (A. L. Spek, PLATON, University of Urecht, The Netherlands, **1999**).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146117 **1**, CCDC-146118 **2**, CCDC-146119 **3**, CCDC-146120 **4**, CCDC-146121 **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[23] One example of an N3-co-ordinated guanine derivative has been isolated which will be described elsewhere, A. Houlton, unpublished results.

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