

Conserved supramolecular architecture in polymetallic nucleobase complexes

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Dedicated to D.M.P. Mingos.

Abstract

The single crystal X-ray structures of two different polynuclear metal–nucleobase complexes are reported. Crystals isolated from the reaction of CdBr_2 with ethylenediamine-N9-ethyladenine, A-Et-en, were characterised by X-ray structural analysis as a coordination polymer $[\mu\text{-}\{\text{CdBr}(\text{N}3,\text{N}7\text{-A-Et-en})\}_2\text{CdBr}_4]$ (**2**). Reaction of the Pd(II)–adenine complex, $[\text{PdCl}(\text{N}3\text{-A-Et-en})]^+$, with sodium uracilate yielded $[(\text{Pd}(\text{N}3\text{-A-Et-en})_2(\text{N}1,\text{N}3\text{-U}))][\text{ClO}_4]_2$ (**3**). Despite the considerable differences in the nature of the compounds the crystal structures feature essentially similar supramolecular architectures. A building block analysis demonstrates how this arises and reveals an approach, based on bond-type substitution and molecular replacement, to conserving such features. This may be a useful approach that could be more widely adopted in crystal engineering strategies.

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1. Introduction

Control of solid-state supramolecular architectures through designed interactions has developed into an increasingly sophisticated science [1–3]. A number of strategies for crystal engineering have been advanced including those based on molecular recognition [4], shape and volume ratios [4–8], and electrostatic templating [9]. Exploiting the vectorial nature of hydrogen bonding is another approach, which has been developed for organic compounds [2,10–12] and also for coordination compounds, particularly by Mingos [13–15]. The combination of metal–ligand bond formation and a hydrogen-bonding periphery has been shown to be an effective way to control molecular association, particularly in the solid state [13–15].

Metal–nucleobase complexes are interesting compounds in this regard since they can exhibit a variety of metal–ion binding modes along with an extensive range of hydrogen bonding patterns [16]. In our work, for instance, we have noted that inter-nucleobase hydrogen-bonding dominates in the crystal structures of metal complexes of N3-bound adenine [17–19], though only in the presence of the complementary base thymine is the base pairing motif readily predictable [20].

A rare exception to these findings is seen in the recently reported Cd-containing coordination polymer derived from adenine $[\{\text{Cd}_2\text{Cl}_6(\text{A-Et-en})_2\}_n]$ (**1**) (A-Et-en = ethylenediamine-N9-ethyladenine) [21]. The extended polymer chains arise from the central bridging $\{\text{CdCl}_4\}^{2-}$ units binding N7 of *trans*-oriented adenines. This gives rise to near parallel adenines, which form part of an open-box motif along the coordination polymer chain (Fig. 1). Here we report two new metal–adenine complexes, both containing the ligand system, ethylenediamine-N9-ethyladenine A-Et-en,

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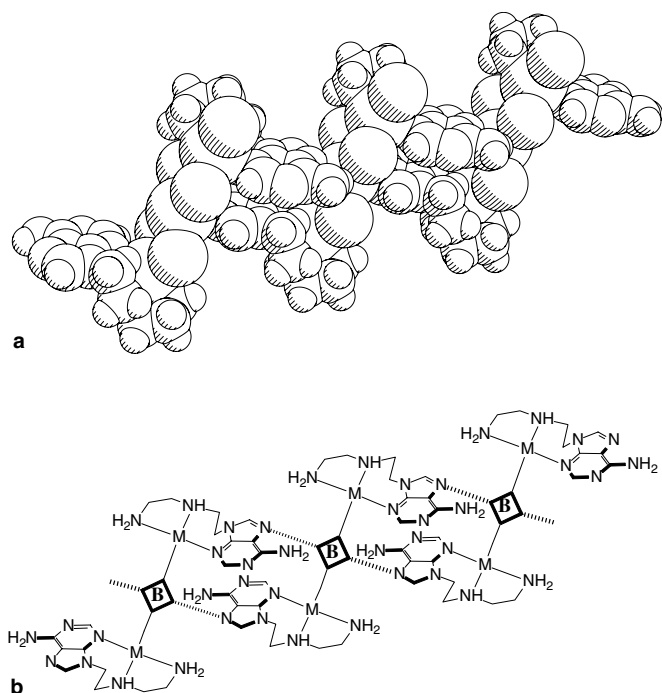


Fig. 1. Space-filling and schematic representations of the adeninyl polymer **1** illustrating the solid-state supramolecular architecture which features near parallel adenines and orthogonally related metal-containing groups as sides of an open-box which form a 1D chain. The bridging unit **B** is $[\text{CdCl}_4]^{2-}$.

as in **1**. These are the bromide analogue of **1**, compound **2**, and a dinuclear Pd(II) complex containing a uracilate-bridging anion **3**. Despite the markedly different compositions of these materials single-crystal X-ray structure analysis reveals that they exhibit essentially the same crystal organization in geometrical terms. The compounds thus highlight the possibility of bond-type substitution and molecular replacement as approaches to conserving supramolecular assemblies.

2. Experimental

The ligand, ethylenediamine-N9-ethyladenine A-Et-en, was prepared as its hydrochloride salt as previously described [17].

2.1. Preparation of compound 2

Compound **2** was prepared from an aqueous solution containing CdBr_2 (0.2 mmol) to which was added an equimolar aqueous solution of A-Et-enH · Cl with stirring. The solution was allowed to stand at room temperature and crystals suitable for single-crystal X-ray analysis were obtained.

2.2. Preparation of compound 3

To a solution of $[\text{Pd}(\text{A-Et-en})\text{Cl}]\text{PF}_6$ [18] in DMF was added an equimolar solution of sodium uracilate in water. The yellow solution was heated to 80 °C with stirring for 2 days. The solvent was removed on a rotary evaporator and the remaining yellow solid was dissolved in distilled water. Any insoluble material was filtered off and the filtrate was concentrated and allowed to stand for 24 h, after which a yellow solid precipitated; this was collected by filtration and air-dried. Initial attempts to obtain crystals suitable for X-ray analysis by recrystallization of the crude material were unsuccessful. Eventually, crystals of **3** suitable for X-ray studies were grown via slow evaporation of an aqueous solution saturated with sodium perchlorate. Satisfactory elemental analysis was not obtained due to decomposition of the crystals.

2.3. Crystallography

A summary of the crystallographic experimental parameters for compounds **2** and **3** is given in Table 1. Data were collected on Bruker SMART 1 K CCD diffractometers using either graphite-monochromated Mo $\text{K}\alpha$ (**3**) or silicon[111]-monochromated synchrotron radiation (**2**) and recorded using ω -scans with narrow frames. SMART and SAINT [22] [a] were used for data collection and integration respectively, with absorption and intensity decay corrections by SADABS [23]. Structure solution was by direct methods with anisotropic refinement for all non-hydrogen atoms by full-matrix least-squares on F^2 using SHELXTL [24], which was also used for graphics. Hydrogen atoms were constrained to ride on the parent atom with $\text{N-H} = 0.88\text{--}0.93 \text{ \AA}$, $\text{C-H} = 0.95\text{--}0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$; H atoms were not located for the water molecules in **3**. This structure showed disorder of water molecules and perchlorate anions. For both structures, the major residual electron density features lie close to heavy atoms and disordered groups.

3. Results and discussion

3.1. Compound 2 $[\mu\text{-}\{\text{CdBr}(\text{N3,N7-A-Et-en})\}_2\text{CdBr}_4]$

To establish whether the lack of inter-nucleobase hydrogen bonding identified in **1** was an isolated case [21] the Br^- analogue, $[\{\text{Cd}_2\text{Br}_6(\text{A-Et-en})_2\}_n]$ (**2**), was also prepared. This involved reaction of CdBr_2 with the adeninyl-diamine ligand, A-Et-en, in aqueous solution. Crystals isolated from the reaction mixture showed that the material was indeed isostructural with the chloride complex **1**. The molecular structure of **2** is shown in Fig. 2. Selected bond lengths and angles are given in Table 2. The structure contains two unique Cd ions, both of which adopt octahedral geometries, though in the case of Cd2 this is considerably distorted. The ligating groups at Cd2 include the A-Et-en acting as a tridentate ligand through the diamine group

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