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Synthesis of 2,6-di(pyrazol-1-yl)-4-bromomethylpyridine, and its conversion to other 2,6-di(pyrazol-1-yl)pyridines substituted at the pyridine ring

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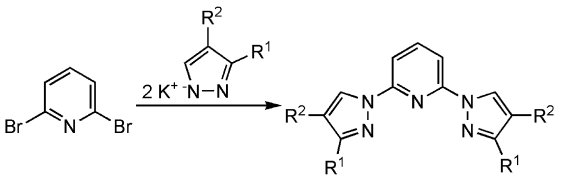
Abstract—Two routes to 2,6-di(pyrazol-1-yl)-4-hydroxymethylpyridine (**1**) from 2,6-dihydroxy-*iso*nicotinic acid, in four and six steps, are reported. Reaction of **1** with 48% HBr yields 2,6-di(pyrazol-1-yl)-4-bromomethylpyridine (**2**), which is a powerful precursor to a range of new tridentate ligands for transition metals functionalised at the pyridine ring. As a proof of principle, we describe the further elaboration of **2** to give two 2,6-di(pyrazol-1-yl)pyridines bearing nucleobase substituents, and the back-to-back ligand 1,2-bis[2,6-di(pyrazol-1-yl)pyrid-4-yl]-ethane. Crystal structures of two of these new derivatives are presented.

1. Introduction

We have been studying the metal complex chemistry of 2,6-di(pyrazol-1-yl)pyridine and 2,6-di(pyrazol-1-yl)pyrazine ligands for some time.[1] The iron(II) complexes of these ligands have proved to be particularly fruitful, in that they undergo thermal spin-crossover transitions at accessible temperatures (typically 200–300 K), which are amenable to detailed study.[2–6] Materials that undergo spin-crossover near room temperature are of great current interest, because their thermochromism lends itself to a variety of applications in display and information storage devices.[7] Others have also found 2,6-dipyrazolylpyridine derivatives to be effective sensitisers for lanthanide ions, which have been incorporated into sensors for biological molecules.[8,9] Synthesis of 2,6-di(pyrazol-1-yl)pyridine derivatives bearing alkyl or substituents at the 3- or 4-positions of the pyrazole ring is generally straightforward, and achieved in no more than three steps from commercially available starting materials. The key step here is the nucleophilic coupling of pre-formed pyrazoles with 2,6-dibromopyridine (Eq. 1), yielding the final tridentate ligand in yields of 50–70%.[10]



(1)

The synthesis of 2,6-di(pyrazol-1-yl)pyridines substituted at the pyridine ring is more difficult,[1] because of the poorer availability of many suitable 4-substituted-2,6-dibromopyridine reagents and because yields of Eq. 1 can be drastically reduced when carried out using 2,6-dibromopyridines bearing electron-withdrawing substituents.[8] Palladium catalysis of Eq. 1 increases the rate of reaction, but does not significantly improve the yields obtained.[11]

We[5] and others[12] have recently addressed this problem by using commercially available 2,6-dihydroxy-*iso*nicotinic acid as a precursor to new 4-substituted-2,6-dibromopyridine derivatives. We report here in full two synthetic pathways to 2,6-di(pyrazol-1-yl)-4-hydroxymethylpyridine (**1**) from this starting material, and its conversion to 2,6-di(pyrazol-1-yl)-4-bromomethylpyridine (**2**). Compound **2** is a potentially useful precursor to other 4-substituted-2,6-di(pyrazol-1-yl)pyridine derivatives bearing a range of pendant substituents. These might be designed to incorporate redox-active or fluorescent substituents onto their complex compounds to dope them onto solid supports, or to link coordinated metal centres covalently or through supramolecular interactions. As a proof of principle, we also describe the synthesis of three new ligands derived from **2** intended for the latter application.

2. Results and discussion

The synthesis of **1** was achieved by two different routes, shown as A and B in Scheme 1. Steps (i), (ii) and (v) of this scheme followed literature procedures.[13,14] While method A is shorter, step (iii) proceeds in a relatively low

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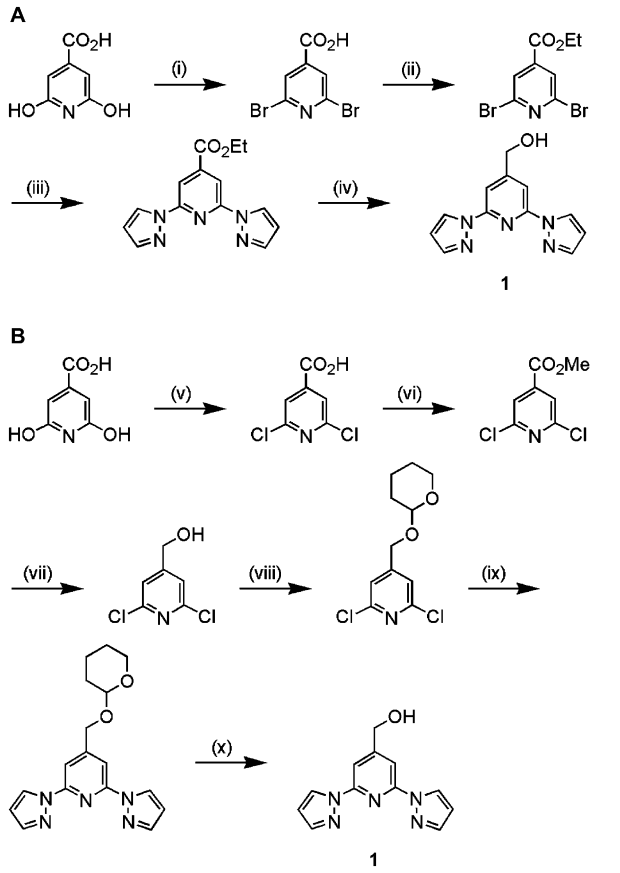
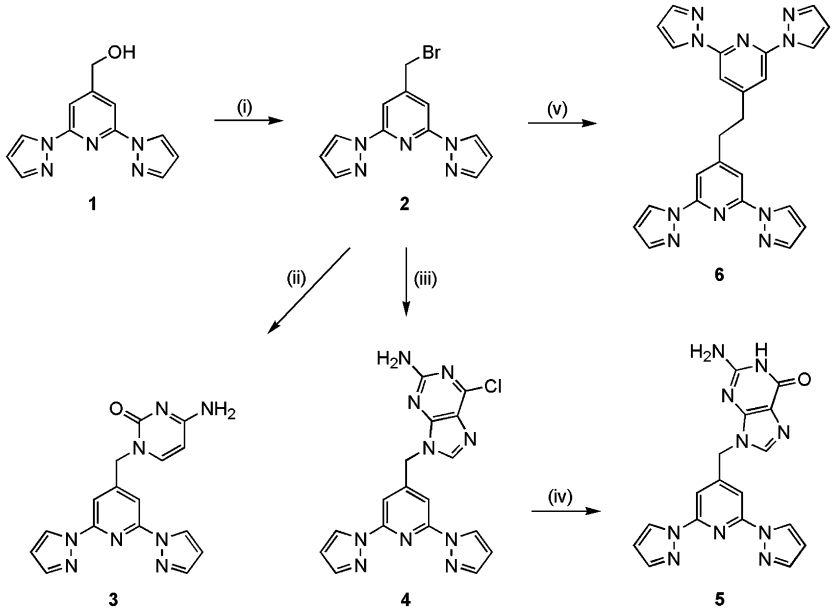


Scheme 1. The two syntheses of **1** used in this study. Reagents and conditions: (i) $POBr_3$, 130 °C, 3 h, 82%; (ii) EtOH, concd H_2SO_4 (cat.), reflux, 15 h, 93%; (iii) 2 equiv Kpz, 2-methoxyethylether, 130 °C, 5 days, 40%; (iv) 5 equiv $NaBH_4$, EtOH, reflux, 3 h, 78%; (v) $POCl_3$, 150 °C, 24 h, 72%; (vi) MeOH, concd H_2SO_4 (cat.), reflux, 15 h, 84%; (vii) 5 equiv $NaBH_4$, EtOH, reflux, 3 h, 85%; (viii) 3,4-dihydropyran, pyridinium *para*-toluenesulfonate, CH_2Cl_2, rt, 16 h, 80%; (ix) 2 equiv Napz, 2-methoxyethylether, 130 °C, 5 days, 81%; (x) pyridinium *para*-toluenesulfonate, EtOH, 55 °C, 3 h, 80%.

yield of 37%, and was also somewhat unreliable in our hands. Although it involves extra protection and deprotection steps, we have found route B in Scheme 1 to be higher yielding and more reliable overall. It also has the advantage of avoiding the expensive reagent $POBr_3$ used to prepare the 2,6-dibromoisonicotinic acid ethyl ester starting material for route A (attempts to perform step (iii) using 2,6-dichloroisonicotinic acid ethyl ester were unsuccessful). Using route B, **1** can be reliably prepared on a multi-gram scale. Bromination of **1** proceeds readily in 48% HBr, yielding **2** in 73% yield after the usual work-up (Scheme 2).

As a proof of principle, we have pursued the synthesis of new ligands bearing nucleobase groups, which could have use in metal-containing host–guest complexes. The only related nucleobase/polyimine conjugates, we are aware of in the literature, are the nucleobase-containing 2,2-bipyridine derivatives prepared by Ward et al. to promote photo-energy transfer between supramolecularly linked donors and acceptors in solution,[15] and a thymine-substituted 2,2:6′,2″-terpyridine communicated by Constable.[16] Deprotonation of cytosine with NaH, and reaction of the resultant anion with **2** in the presence of catalytic KI, cleanly affords **3** in 69% yield. However similar reactions using guanine, adenine or thymine all yielded mixtures of products containing both mono- and di-alkylated nucleobases by ^{1}H NMR, which were not amenable to separation because of their poor solubilities in solvents other than DMSO. This problem was overcome in the guanine case by reaction of **2** with 2-amino-6-chloropurine, cleanly yielding the monoalkylation product **4**, which was in turn dechlorinated to **5** by acid hydrolysis.[17] Although pure by NMR, as-precipitated **5** appears to retain some water upon drying by microanalysis. This suggestion was supported by its ES mass spectrum, which contained a strong peak at m/z=393 assignable to $[M+H_2O+H]^+$.

Pale yellow plates of formula $[\mathbf{3}_2H]ClO_4$ crystallised from a $MeNO_2/Et_2O$ solution of **3** and $Fe[ClO_4]_2\cdot 6H_2O$.



Scheme 2. Conversion of **1** to **2**, and the further derivatisation of **2**. Reagents and conditions: (i) 48% HBr, reflux, 4 h, 73%; (ii) Na[cytosinate], KI (cat.), DMF, 50 °C, 5 h, 69%; (iii) Na[9-chloroguaninate], KI (cat.), DMF, 50 °C, 5 h, 95%; (iv) 0.1 M HCl, reflux, 4 h, 67%; (v) BuLi, Et_2O, −78 °C then 1,2-dibromoethane, rt, 24 h, 50%.

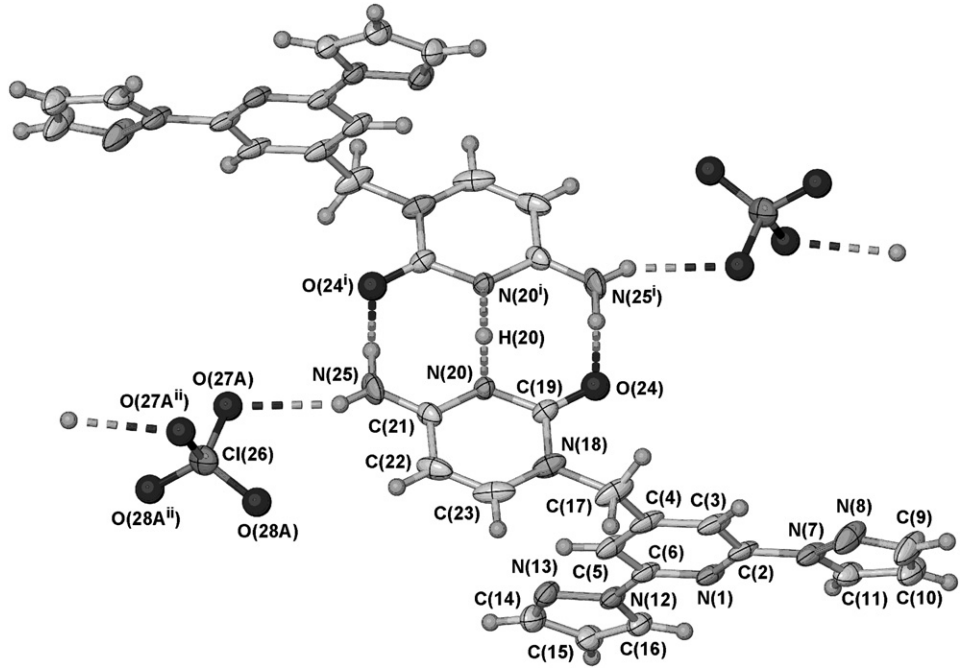


Figure 1. Partial packing diagram of $[\mathbf{3}_2H]ClO_4$, showing the protonated dimeric supramolecules in the lattice and their association with the perchlorate anions. Thermal ellipsoids are at the 50% probability level, except for H atoms, which have arbitrary radii. For clarity, only one orientation of the (disordered) ClO_4^- anion is shown. Symmetry codes: (i) $1/2-x$, $3/2-y$, $1-z$; (ii) $-x$, y, $1/2-z$.

Presumably, the proton in this compound originated from the weakly acidic $MeNO_2$ solvent. The structure contains a centrosymmetric dimeric supramolecule of **3**, with their two cytosine moieties linked by two N–H···O hydrogen bonds (Fig. 1). The two N3 atoms of these groups are spanned by a shared proton [H(20) in Fig. 1], which lies on the crystallographic inversion centre in the structural refinement. This supramolecular motif has been seen before in other $[(Cyt)_2H]^+$ (cyt=cytosine or a 1-alkylcytosine derivative) co-crystals.[18–20] In contrast to at least one previous example,[19] the $[(Cyt)_2H]^+$ moiety in $[\mathbf{3}_2H]^+$ is perfectly coplanar. The dimeric supramolecules are linked into 1-D chains running parallel to the crystallographic [101] vector, through hydrogen bonding to the perchlorate anions (Fig. 1). The cytosinyl and 2,6-di(pyrazol-1-yl)pyrid-4-yl groups in each molecule of **3** are mutually close to perpendicular, with a dihedral angle of 76.67(5)° between their least squares planes. The 1-D chains in the lattice therefore form a set of approximately square cavities, with two adjacent sides formed from $[(Cyt)_2H]^+$ protonated dimers, and the other two by 2,6-di(pyrazol-1-yl)pyrid-4-yl groups. These cavities have approximate dimensions $3.7\times3.9\times8.3$ Å, and are filled by two more 2,6-di(pyrazol-1-yl)pyrid-4-yl substitutents held in place by π–π interactions with the $[(Cyt)_2H]^+$ groups (Fig. 2). Since the space-filling heterocyclic groups are attached to different neighbouring hydrogen-bonded chains, this motif does not result in a self-penetrating network. The pyrazole and pyridine rings in **3** adopt the near-coplanar, *transoid* conformation that is usually observed in crystals of 2,6-di(pyrazol-1-yl)pyridine derivatives (Fig. 1).[1,21]

Lithiation of **2** at −78 °C in diethyl ether, followed by stirring at room temperature for 24 h, yielded the back-to-back ligand **6** in variable yields of up to 50% (Scheme 2). Addition of the oxidising agent 1,2-dibromoethane to the reaction appeared to improve its reliability, without significantly increasing the yield obtained. Related syntheses of 1,2-bis(pyrid-4-yl)ethane by the oxidative lithiation of

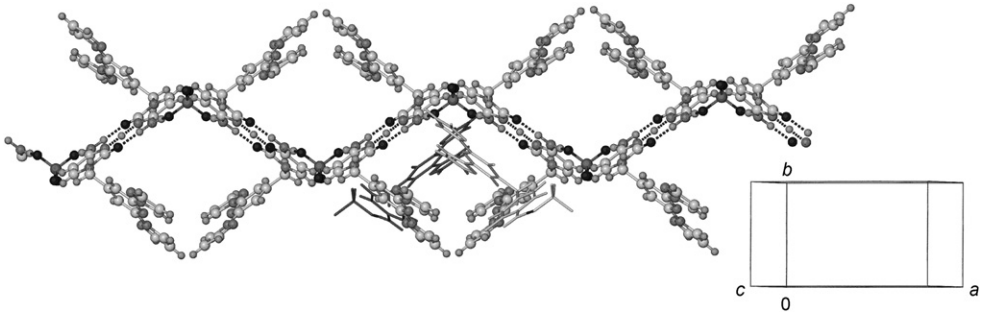


Figure 2. Partial packing diagram of $[\mathbf{3}_2H]ClO_4$, showing the approximately square cavities formed by the hydrogen-bonded chains of molecules. All atoms have arbitrary radii, while the two 2,6-di(pyrazol-1-yl)pyrid-4-yl substitutents filling one of the cavities are also shown, and de-emphasised. The orientation of the unit cell in the view is shown in inset (not to scale).

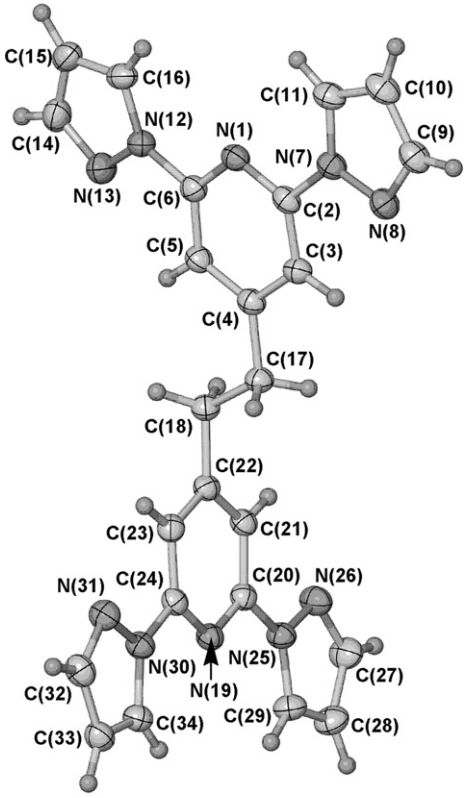
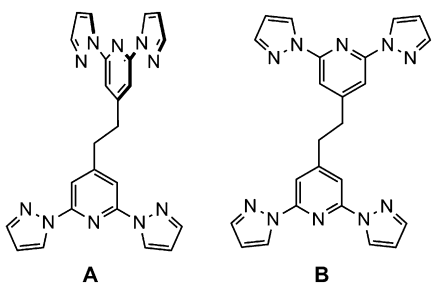


Figure 3. Structure of the whole unique molecule in the crystal of **6**·2/3CH_2Cl_2. Thermal ellipsoids are at the 50% probability level, except for H atoms, which have arbitrary radii. The second half molecule in the structure is similar, but has coplanar 2,6-di(pyrazol-1-yl)pyrid-4-yl substitutents rather than near-perpendicular ones as here.

4-picoline have been reported previously.[22] While the identity of **6** was confirmed by NMR and mass spectrometry, microanalysis consistently implied that the recrystallised product also contained lattice solvent. That was confirmed by a structure determination from a crystal of stoichiometry **6**·2/3CH_2Cl_2 (Fig. 3). These crystals contain one whole molecule (molecule 'A') and one centrosymmetric half molecule (molecule 'B') of **6**, which differ in the relative dispositions of their two 2,6-di(pyrazol-1-yl)pyrid-4-yl fragments (Scheme 3). In the whole molecule these moieties are almost perpendicular to each other, with a dihedral angle between their least squares planes of 83.12(2)° (Fig. 3), while in the half molecule (not shown in Fig. 3) they are strictly coplanar by symmetry. As for [$\mathbf{3}_2$H]ClO_4, the three heterocycles in each of the unique 2,6-di(pyrazol-1-yl)pyrid-4-yl moieties in **6**·2/3CH_2Cl_2 all exhibit the usual near-coplanar, *transoid* conformation.[1,21] The two unique molecules of **6** in the crystal associate through π–π interactions into centrosymmetric BAAB tetrads zigzagging along the unit cell *b* direction (via the symmetry transformation $1-x$, $-y$, $1-z$), while the remaining 2,6-di(pyrazol-1-yl)pyrid-4-yl fragment in molecule A also forms a centrosymmetric π–π interaction with its own symmetry equivalent related by $-x$, $-y$, $2-z$.



Scheme 3. Different conformations of molecule A and half molecule B in the crystal structure of **6**·2/3CH_2Cl_2. Molecule A is shown in Figure 3.

3. Conclusions

This work has demonstrated that **2** can be a powerful precursor to a range of 2,6-di(pyrazol-1-yl)pyridines substituted at the pyridyl group, which could allow spin-transition centres to be linked together, to be combined with other functionality in the same molecule, or to be tethered onto surfaces. While we have studied the iron(II) complexes of **1**[5,6] and **2**[23] in some detail, unfortunately **3**, **5** and **6** are of limited value as ligands in themselves since their homoleptic iron(II) complexes are intractably insoluble and non-crystalline. The amorphous nature of the complexes is also reflected in the spin transitions they undergo upon cooling,[1] which are extremely gradual and proceed to <50% completion.[23] None-the-less, there is very wide scope for conversion of **2** into a wide range of other tridentate ligands bearing pendant functionality, whose iron complexes may behave more promisingly. The solubility and crystallinity problems referred to above might also be alleviated by preparing analogues of **3**, **5** and **6** bearing alkyl substituents at the 4-positions of the pyrazole rings in steps (iii) or (ix) of Scheme 1 (cf. Eq. 1, $R^2 \neq H$). We are actively investigating all these possibilities.

4. Experimental

4.1. General

2,6-Dibromoisonicotinic acid ethyl ester[13] and 2,6-dichloroisonicotinic acid[14] were prepared by the literature procedures. All other reactions were carried out in air using non-pre-dried AR-grade solvents unless otherwise stated, and all reagents were purchased commercially and used as supplied. Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. NMR spectra were obtained on a Bruker ARX250 spectrometer, operating at 250.1 MHz (^{1}H) and 62.9 MHz (^{13}C). Electron impact mass spectra were obtained on a VG Autospec instrument, while electrospray mass spectra were run from MeCN solution using a Micromass LCT TOF spectrometer. Melting points are uncorrected. [CAUTION: While we have experienced no difficulty in handling the iron complexes described below, metal-organic perchlorates are potentially explosive and should be handled with due care in small quantities.]

4.2. Syntheses

4.2.1. 2,6-Di(pyrazol-1-yl)isonicotinic acid ethyl ester. A solution of pyrazole (5.80 g, 86 mmol) in 2-methoxyethylether (300 mL) was added to solid KH (3.55 g, 89 mmol) under N_2, and the resultant suspension stirred at room temperature for 1 h. 2,6-Dibromoisonicotinic acid ethyl ester

(8.50 g, 28 mmol) was then added in one portion, and the mixture stirred at 130 °C for 5 days. After cooling, a large excess of cold water was added to the mixture, yielding a white solid, which was collected and washed with water. Yield 3.1 g, 40%. Found C, 59.4; H, 4.7; N, 24.6%. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.4; H, 4.6; N, 24.7%. Mp 147–149 °C (lit.[13] 143–144 °C). EI mass spectrum: *m/z* 284 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 8.50 (d, 2.2 Hz, 2H, Pz H^5), 8.32 (s, 2H, Py $H^{3/5}$), 7.74 (d, 1.7 Hz, 2H, Pz H^3), 6.46 (dd, 1.7 and 2.2 Hz, 2H, Pz H^4), 4.40 (q, 7.1 Hz, 2H, CH_2), 1.39 (t, 7.1 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.0 (1C, CO_2), 150.7 (2C, Py $C^{2/6}$), 143.6 (1C, Py C^4), 142.7 (2C, Pz C^3), 127.1 (2C, Pz C^5), 109.1 and 108.3 (both 2C, Py $C^{3/5}$ and Pz C^4), 62.1 (1C, CH_2), 14.2 (1C, CH_3).

4.2.2. 2,6-Dichloroisonicotinic acid methyl ester. A solution of 2,6-dichloroisonicotinic acid (16.5 g, 86 mmol) in MeOH (135 mL) was treated with concd H_2SO_4 (1.2 mL) and refluxed for 15 h. After the mixture was cooled to room temperature, a brown solid precipitated and was collected. Yield 14.9 g, 84%. Mp 71–73 °C (lit.[24] 80–81 °C). Found C, 40.8; H, 2.6; N, 6.7%. Calcd for $C_7H_5NO_2Cl_2$: C, 40.8; H, 2.5; N, 6.8%. EI mass spectrum: *m/z* 206 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ 7.77 (s, 2H, Py $H^{3/5}$), 3.95 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 163.2 (1C, CO_2Me), 151.4 (2C, Py $C^{2/6}$), 142.4 (1C, Py C^4), 122.6 (2C, Py $C^{3/5}$), 53.3 (1C, CH_3).

4.2.3. 2,6-Dichloro-4-hydroxymethylpyridine. $NaBH_4$ (5.70 g, 0.15 mol) was added in portions to a solution of 2,6-dichloro-4-ethoxycarbonylpyridine (6.25 g, 30 mmol) in dry EtOH (570 mL) at 0 °C. The mixture was then heated to reflux for 3 h under N_2 atmosphere. The resultant solution was then cooled, and evaporated to dryness. The residue was taken up in H_2O (430 mL), and excess $NaBH_4$ was destroyed by the addition of 1 M HCl (110 mL). The mixture was neutralised with Na_2CO_3 and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and solvent was removed, affording a pale brown solid. Yield 4.5 g, 85%. Mp 129–131 °C (lit.[25] 133 °C). Found C, 40.5; H, 3.1; N, 7.9%. Calcd for $C_6H_5NOCl_2$: C, 40.5; H, 2.8; N, 7.9%. EI mass spectrum: *m/z* 178 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 7.21 (s, 2H, Py $H^{3/5}$), 4.68 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 160.0 (2C, Py $H^{2/6}$), 149.4 (1C, Py C^4), 120.9 (2C, Py $C^{3/5}$), 61.1 (1C, CH_2).

4.2.4. 2,6-Dichloro-4-(tetrahydropyran-2-yloxymethyl)-pyridine. A solution of pyridinium *para*-toluenesulfonate (1.05 g, 4.4 mmol) in CH_2Cl_2 (30 mL) was added dropwise with stirring, at room temperature, to a solution of 2,6-dichloro-4-hydroxymethylpyridine (3.75 g, 21 mmol) and 3,4-dihydropyran (3.69 g, 44 mmol) in CH_2Cl_2 (600 mL). The mixture was stirred at room temperature overnight. The solvent was then removed in vacuo, and Et_2O was added (300 mL). The solution was extracted with water, separated, dried over $MgSO_4$ and concentrated in vacuo. Silica flash column chromatography in 85:15 pentane/Et_2O afforded the pure product as a white solid. Yield 4.4 g, 80%. Mp 59–61 °C. Found C, 50.6; H, 5.1; N, 5.2%. Calcd for $C_{11}H_{13}NO_2Cl_2$: C, 50.4; H, 5.0; N, 5.3%. EI mass spectrum: *m/z* 262 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 7.18 (s, 2H, Py $H^{3/5}$), 4.41 and 4.70 (both d, 15.1 Hz, both 1H, pyCH_2O), 4.64 (t, 3.2 Hz, 1H, pyran C*H*), 3.49 and 3.76 (both m, both 1H, pyran CH_2 ^{6}), 1.42–1.93 (m, 6H, pyran CH_2 $^{3-5}$). ^{13}C NMR ($CDCl_3$): δ 154.4 (2C, Py $C^{2/6}$), 151.0 (1C, Py C^4), 121.1 (2C, Py $C^{3/5}$), 98.9 (1C, pyran C*H*), 66.5, 62.9 (both 1C, pyCH_2O and pyran CH_2 ^{6}), 20.1, 25.6 and 30.7 (all 1C, pyran CH_2 $^{3-5}$).

4.2.5. 2,6-Di(pyrazol-1-yl)-4-(tetrahydropyran-2-yl-oxymethyl)pyridine. A solution of pyrazole (3.19 g, 47 mmol) in 2-methoxyethylether (170 mL) was added to NaH (1.12 g, 47 mmol) under N_2, and the resultant suspension stirred at room temperature for 1 h. 2,6-Dichloro-4-tetrahydropyranyloxypyridine (4.20 g, 16 mmol) was then added to the reaction in one portion, and the mixture stirred at 130 °C for 5 days. After cooling, a large excess of cold water was added to the mixture, yielding a brown oil that was collected by decantation, washed with water and dried in vacuo. Any 2-methoxyethylether remaining in the product by NMR was removed with additional aqueous washes. Yield 4.2 g, 81%. Found C, 63.1; H, 5.8; N, 21.8%. Calcd for $C_{17}H_{19}N_5O_2$: C, 62.8; H, 5.9; N, 21.5%. EI mass spectrum: *m/z* 326 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 8.48 (d, 3.3 Hz, 2H, Pz H^5), 7.79 (s, 2H, Py $H^{3/5}$), 7.68 (d, 1.7 Hz, 2H, Pz H^3), 6.40 (dd, 1.7 and 3.3 Hz, 2H, Pz H^4), 4.55 and 4.83 (both d, 14.0 Hz, both 1H, pyCH_2O), 4.70 (t, 3.4 Hz, 1H, pyran C*H*), 3.48 and 3.82 (both m, both 1H, pyran CH_2 ^{6}), 1.45–1.96 (m, 6H, pyran CH_2 $^{3-5}$). ^{13}C NMR ($CDCl_3$): δ 154.6 (2C, Py $C^{2/6}$), 150.6 (1C, Py C^4), 142.6 (2C, Pz C^5), 127.5 (2C, Pz C^3), 107.9 and 108.3 (both 2C, Py $C^{3/5}$ and Pz C^4), 98.8 (1C, pyran C*H*), 62.4 and 67.6 (both 1C, pyCH_2O and pyran CH_2 ^{6}), 19.5, 25.8 and 30.8 (all 1C, pyran CH_2 $^{3-5}$).

4.2.6. 2,6-Di(pyrazol-1-yl)-4-(hydroxymethyl)pyridine (1). *Method A*: Solid $NaBH_4$ (1.75 g, 46 mmol) was added in portions to a solution of 2,6-di(pyrazol-1-yl)isonicotinic acid ethyl ester (2.63 g, 9.3 mmol) in anhydrous ethanol (190 mL) at 0 °C. After the addition was complete, the mixture was heated to reflux under N_2 for 3 h. The solution was cooled to room temperature, and evaporated to dryness. Water (140 mL) was added to the residue, and excess $NaBH_4$ was destroyed by the addition of 1 M HCl (35 mL). The mixture was then neutralised with Na_2CO_3, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated to dryness, affording a bright brown solid product. Yield 1.74 g, 78%. *Method B*: A solution of 2,6-bis(pyrazol-1-yl)-4-tetrahydropyranyloxypyridine (3.85 g, 12 mmol) and PPTS (0.29 g, 1.2 mmol) in EtOH (100 mL) was stirred at 55 °C for 3 h. The solvent was then removed in vacuo, and the residue redissolved in Et_2O (80 mL). The solution was extracted with water, separated, dried over $MgSO_4$ and concentrated in vacuo to yield a white solid that was used without further purification. Yield 2.3 g, 80%. Found C, 60.0; H, 4.6; N, 29.0%. Calcd for $C_{12}H_{11}N_5O$: C, 59.7; H, 4.6; N, 29.0%. Mp 128–130 °C. EI mass spectrum: *m/z* 242 $[M+H]^+$. ^{1}H NMR ($CDCl_3$): δ 8.50 (d, 2.6 Hz, 2H, Pz H^5), 7.82 (s, 2H, Py $H^{3/5}$), 7.72 (d, 1.7 Hz, 2H, Pz H^3), 6.45 (dd, 1.7 and 2.6 Hz, 2H, Pz H^4), 4.81 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 157.0 (2C, Py $C^{2/6}$), 150.0 (1C, Py C^4), 142.3 (2C, Pz C^3), 127.2 (2C, Pz C^5), 107.9 and 106.7 (both 2C, Py $C^{3/5}$ and Pz C^4), 63.3 (1C, CH_2).

4.2.7. 2,6-Di(pyrazol-1-yl)-4-(bromomethyl)pyridine (2). Compound **1** (2.75 g, 11 mmol) was refluxed in 48% HBr

(70 mL) for 4 h. The mixture was then cooled to room temperature, poured onto 40 g of ice, made basic with a saturated solution of Na_2CO_3, and extracted with CH_2Cl_2 (4×50 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under vacuum, yielding a light brown solid. Pure product was isolated by flash silica column chromatography in 4:1 pentane/ether. Yield 2.54 g, 73%. Found C, 47.4; H, 3.5; N, 22.6%. Calcd for $C_{12}H_{10}N_5Br$: C, 47.2; H, 3.6; N, 22.9%. Mp 130–132 °C. EI mass spectrum: *m/z* 306 [$M(^{81}Br)$+H]$^+$, 304 [$M(^{79}Br)$+H]$^+$. ^{1}H NMR ($CDCl_3$): δ 8.51 (d, 2.4 Hz, 2H, Pz H^5), 7.86 (s, 2H, Py $H^{3/5}$), 7.74 (d, 1.6 Hz, 2H, Pz H^3), 6.46 (dd, 1.6 and 2.5 Hz, 2H, Pz H^4), 4.45 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 152.1 (2C, Py $C^{2/6}$), 150.5 (1C, Py C^4), 142.6 (2C, Pz C^3), 127.1 (2C, Pz C^5), 109.3, 108.1 (both 2C, Py $C^{3/5}$ and Pz C^4), 30.0 (1C, CH_2).

4.2.8. 1-([2,6-Di(pyrazol-1-yl)pyridin-4-yl]methyl)cytosine (3). A solution of cytosine (0.11 g, 1.0 mmol) and a catalytic amount of KI (0.030 g) in dry DMF (10 mL) was added to NaH (0.024 g, 1.0 mmol) at 0 °C under N_2. The mixture was stirred for 30 min at room temperature, and a solution of **2** (0.31 g, 1.0 mmol) in dry DMF (10 mL) was then added and the mixture stirred for 5 h at 50 °C under N_2. After cooling to room temperature, addition of water (100 mL) afforded a white precipitate. This was collected, dried in vacuo over P_2O_5 and analysed without further purification. Yield 0.23 g, 69%. Found C, 57.3; H, 4.1; N, 33.1%. Calcd for $C_{16}H_{14}N_8O$: C, 57.5; H, 4.2; N, 33.5%. Mp 308 °C. EI mass spectrum: *m/z* 669 [2*M*+H]$^+$, 335 [*M*+H]$^+$. ^{1}H NMR ({CD_3}$_2$SO): δ 8.92 (d, 2.6 Hz, 2H, Pz H^5), 7.85 (d, 1.7 Hz, 2H, Pz H^3), 7.81 (d, 7.2 Hz, Ct H^6), 7.65 (s, 2H, Py $H^{3/5}$), 7.18 (br s, 2H, NH_2), 6.62 (dd, 1.7 and 2.6 Hz, 2H, Pz H^4), 5.79 (d, 7.2 Hz, Ct H^5), 5.06 (s, 2H, CH_2). ^{13}C NMR ({CD_3}$_2$SO): δ 166.6 (1C, Ct C^4), 162.7 (1C, Ct C^2), 154.5 (2C, Py $C^{2/6}$), 150.1 (1C, Py C^4), 146.6 (1C, Ct C^6), 143.0 (2C, Pz C^3), 128.5 (2C, Pz C^5), 108.9, 107.3 (both 2C, Py $C^{3/5}$ and Pz C^4), 94.5 (1C, Ct C^5), 51.4 (1C, CH_2).

4.2.9. 6-Chloro-9-[2,6-di(pyrazol-1-yl)pyridin-4-yl]-methyl-9*H*-purin-2-ylamine (4). Compound **4** was prepared by the same method as for **3**, using 2-amino-6-chloropurine (0.17 g, 1.0 mmol). The product precipitated as a white solid after the aqueous quench. Yield 0.37 g, 95%. Found C, 51.6; H, 3.7; N, 35.2%. Calcd for $C_{17}H_{13}ClN_{10}$: C, 52.0; H, 3.3; N, 35.6%. Mp 231–233 °C. EI mass spectrum: *m/z* 393 [$M(^{35}Cl)$+H]$^+$. ^{1}H NMR ({CD_3}$_2$SO): δ 9.07 (d, 2.5 Hz, 2H, Pz H^5), 8.50 (s, 1H, Pu H^8), 7.99 (d, 1.7 Hz, 2H, Pz H^3), 7.75 (s, 2H, Py $H^{3/5}$), 7.13 (br s, 2H, NH_2), 6.62 (dd, 1.7 and 2.5 Hz, 2H, Pz H^4), 5.70 (s, 2H, CH_2). ^{13}C NMR ({CD_3}$_2$SO): δ 160.4 (1C, Pu C^6), 154.5 (1C, Pu C^4), 152.9 (2C, Py $C^{2/6}$), 150.3 (1C, Py C^4), 150.1 (1C, Pu C^2), 143.7 (1C, Pu C^8), 143.2 (2C, Pz C^3), 128.6 (2C, Pz C^5), 123.5 (1C, Pu C^5), 108.9 and 107.0 (both 2C, Py $C^{3/5}$ and Pz C^4), 45.8 (1C, CH_2).

4.2.10. 9-[2,6-Di(pyrazol-1-yl)pyridin-4-yl]methylguanine sesquihydrate (5). Compound **4** (0.70 g, 1.8 mmol) was refluxed in 0.1 M HCl (150 mL) for 4 h. After cooling and neutralisation with aq KOH, the product precipitated as a yellow solid, which was filtered and analysed without further purification. Yield 0.47 g, 67%. Found C, 51.2; H, 4.0; N, 35.2%. Calcd for $C_{17}H_{14}N_{10}O\cdot1.5H_2O$: C, 50.9; H, 4.3; N, 34.9%. Mp 217–219 °C. EI mass spectrum: *m/z* 749 [2*M*+H]$^+$, 393 [*M*+H_2O+H]$^+$, 374 [*M*]$^+$. ^{1}H NMR ({CD_3}$_2$SO): δ 9.03 (d, 2.5 Hz, 2H, Pz H^5), 8.47 (s, 1H, Gu H^8), 7.96 (d, 1.7 Hz, 2H, Pz H^3), 7.71 (s, 2H, Py $H^{3/5}$), 7.09 (br s, 2H, NH_2), 6.74 (dd, 1.7 and 2.5 Hz, 2H, Pz H^4), 5.66 (s, 2H, CH_2). ^{13}C NMR ({CD_3}$_2$SO): δ 160.4 (1C, Gu C^6), 154.5 (1C, Gu C^4), 152.8 (2C, Py $C^{2/6}$), 150.3 (1C, Gu C^2), 150.1 (1C, Py C^4), 143.7 (1C, Gu C^8), 143.2 (2C, Pz C^3), 128.6 (2C, Pz C^5), 123.5 (1C, Gu C^5), 109.0 and 107.0 (both 2C, Py $C^{3/5}$ and Pz C^4), 45.8 (1C, CH_2).

4.2.11. 1,2-Bis[2,6-di(pyrazol-1-yl)pyrid-4-yl]ethane dichloromethane solvate (6). Compound **2** (0.61 g, 2.0 mmol) was suspended in dry diethyl ether (10 mL) under N_2 at −78 °C. Butyllithium (1.25 mL of a 1.6 M solution in hexanes, 2.0 mmol) was then added, and the reaction stirred at −78 °C for 1 h. 1,2-Dibromoethane (0.42 g, 2.0 mmol) was added, and the reaction warmed to room temperature and stirred for 2 h. The mixture was then quenched with water (50 mL), the organic layer was separated and the aqueous layer extracted with dichloromethane (3×30 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure to yield a pale brown solid. Recrystallisation from CH_2Cl_2/pentane yielded a white polycrystalline solid, which was isolated by filtration and dried in vacuo. The presence of CH_2Cl_2 in the product, suggested by microanalysis, was confirmed crystallographically (see below). Yield 0.25 g, 50%. Found C, 59.6; H, 4.2; N, 28.8%. Calcd for $C_{24}H_{20}N_{10}\cdot\frac{1}{2}CH_2Cl_2$: C, 60.0; H, 4.3; N, 28.5%. Mp 183–185 °C. EI mass spectrum: *m/z* 449 [*M*+H]$^+$. ^{1}H NMR ($CDCl_3$): δ 8.55 (d, 2.7 Hz, 4H, Pz H^5), 7.78 (s, 4H, Py $H^{3/5}$), 7.75 (d, 1.7 Hz, 4H, Pz H^3), 6.48 (dd, 1.8 and 2.7 Hz, 4H, Pz H^4), 3.17 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 154.8 (4C, Py $C^{2/6}$), 149.3 (2C, Py C^4), 141.3 (4C, Pz C^3), 126.1 (4C, Pz C^5), 108.2, 106.9 (both 4C, Py $C^{3/5}$ and Pz C^4), 35.2 (2C, CH_2).

4.2.12. [Fe(3)$_2$][ClO$_4$]$_2$. A mixture of Fe[ClO_4]$_2\cdot6H_2O$ (0.11 g, 0.30 mmol) and **3** (0.20 g, 0.60 mmol) in CH_3NO_2 (30 mL) was refluxed for 30 min. The resultant orange solution was cooled to room temperature, then concentrated in vacuo to ca. 10 mL. Storage at room temperature resulted in a mustard yellow powder, that was very sparingly soluble and was analysed without further purification. Yield 0.14 g, 52%. Found C, 41.3; H, 3.3; N, 24.2%. Calcd for $C_{32}H_{28}N_{16}FeCl_2O_{10}$: C, 41.6; H, 3.1; N, 24.3%. ES mass spectrum: *m/z* 823 [^{56}Fe(**3**)$_2^{35}ClO_4$]$^+$, 669 [2(**3**)+H]$^+$, 362 [^{56}Fe(**3**)$_2$]$^{2+}$, 335 [**3**+H]$^+$. IR (Nujol) 3407br, 3325br, 3198br, 1730s, 1688m, 1652s, 1621s, 1545s, 1524s, 1337m, 1356m, 1277m, 1261m, 1208s, 1174m, 1095vs, 1044m, 972m, 955s, 917m, 849m, 801m, 784s, 773s, 754m, 624s cm^{-1}.

4.2.13. [Fe(5)$_2$][ClO$_4$]$_2\cdot$3H$_2$O. This compound was prepared by the method described in 4.2.12, using **5** (0.24 g, 0.60 mmol). The product was a sparingly soluble yellow-brown powder. Yield 0.14 g, 61%. Found C, 38.6; H, 2.9; N, 26.2%. Calcd for $C_{34}H_{28}N_{20}FeCl_2O_{10}\cdot3H_2O$: C, 38.6; H, 3.2; N, 26.5%. ES mass spectrum: *m/z* 749 [2(**5**)+H]$^+$, 547 [^{56}Fe(**5**)(H_2O)^{35}ClO_4]$^+$, 529 [^{56}Fe(**5**)^{35}ClO_4]$^+$, 393 [**5**+H_2O+H]$^+$, 374 [**5**+H]$^+$. IR (Nujol) 3470br, 3330br, 3116br, 1693m, 1613s, 1563s, 1521s, 1507m, 1404m,

1310m, 1282m, 1209m, 1173m, 1095vs, 1048m, 1000m, 971s, 911m, 858w, 785m, 760s, 730m, 643m, 623s, 600m cm^{-1}.

4.2.14. [Fe(6)][ClO_4]$_2$·H_2O. A solution of **6** (0.17 g, 0.39 mmol) in acetone (60 mL) was added dropwise to a solution of Fe[ClO_4]$_2$·6H_2O (0.14 g, 0.39 mmol) in acetone (20 mL), yielding a yellow precipitate. The reaction was stirred for a further 90 min after addition was complete. The pale yellow solid was isolated by filtration, washed at the filter with acetone, dichloromethane and methanol and dried in vacuo. Yield 0.17 g, 59%. Found C, 39.7; H, 3.0; N, 19.2%. Calcd for $C_{24}H_{20}Cl_2FeN_{10}O_8·H_2O$: C, 40.0; H, 3.1; N, 19.4%. IR (Nujol) 3403br, 3116m, 1632s, 1581m, 1524m, 1406m, 1339m, 1287m, 1216w, 1178w, 1095vs, 1058m, 976s, 892w, 870w, 781m, 623m cm^{-1}. The compound was insufficiently soluble to give a detectable ES mass spectrum.

4.3. Single crystal X-ray structure determinations

Crystals of [**3**$_2$H]ClO_4 were obtained serendipitously, from an attempted recrystallisation of [Fe(**3**)$_2$][ClO_4]$_2$ from CH_3NO_2 over a period of several days. Diffraction data for this compound were collected using a Bruker X8 Apex diffractometer, using graphite-monochromated Mo Kα radiation generated by a rotating anode. Single crystals of **6**·2/3CH_2Cl_2 were obtained by slow diffusion of pentane vapour into a CH_2Cl_2 solution of the compound, and were analysed using a Nonius KappaCCD area detector diffractometer, with graphite-monochromated Mo Kα radiation from a sealed tube source. Experimental details from the structure determinations are given in Table 1. The structures were solved by direct methods (SHELXS 97[26]) and refined by full matrix least squares on F^2 (SHELXL 97[27]). All crystallographic figures were prepared using XSEED,[28] which incorporates POVRAY.[29] The CCDC reference numbers for the structures are 617656 ([**3**$_2$H]ClO_4) and 617655 (**6**·2/3CH_2Cl_2).

Table 1. Experimental details for the single crystal structure determinations in this study

	[**3**$_2$H]ClO_4	**6**·2/3CH_2Cl_2
Formula	$C_{32}H_{29}ClN_{16}O_6$	$C_{24.67}H_{21.33}Cl_{1.33}N_{10}$
M_r	769.16	505.12
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	22.066(3)	10.1953(2)
b (Å)	12.4986(13)	12.5985(3)
c (Å)	12.4529(14)	14.8638(4)
α (deg)	—	97.1977(10)
β (deg)	92.455(5)	100.9265(11)
γ (deg)	—	102.4931(9)
V (Å^3)	3431.2(7)	1802.44(7)
Z	4	3
D_c (g cm^{-3})	1.489	1.396
μ (mm^{-1})	0.183	0.233
T (K)	150(2)	150(2)
Measured reflections	34,227	37,949
Independent reflections	3388	8237
R_{int}	0.051	0.095
R(*F*)	0.058	0.048
wR(F^2)	0.182	0.138

4.3.1. Single crystal X-ray structure determination of [$_2$H]ClO_4. The asymmetric unit contains half of a hydrogen-bonded dimer of molecules lying across the inversion centre [1/4, 3/4, 1/2]. The two halves of this dimer share a proton (H20), which lies on this inversion centre, yielding a protonated dimer cation. The asymmetric unit also contains half of a ClO_4^- anion, which is disordered across the crystallographic C_2-axis [0, *y*, 1/4]; the Cl atom Cl(26) was modelled as lying on this axis. Two disorder orientations of the anion O atoms were modelled: O(27A) and O(28A) (occupancy 0.5) form a C_2-symmetric partial anion with their symmetry equivalents and O(27B)–O(30B) (occupancy 0.25) form a complete partial anion environment. Combining partial anions 'A', 'B' and the symmetry equivalent of 'B' yields a complete anion occupancy. All Cl–O bonds were restrained to 1.44(2) Å, and O···O distances within a given disorder orientation to 2.35(1) Å. All non-H atoms except for anion disorder orientation 'B' were refined anisotropically. All H atoms were first located in the difference map, thus confirming the assignments of the N2 and C5 atoms of each pyrazole ring in the structure. For the final refinements, however, the C-bound H atoms were all placed in calculated positions and refined using a riding model. N-bound H(20), H(25A) and H(25B) were refined freely with a common *U*iso thermal parameter of 0.092(9) Å^2. Since H(20) lies on a special position, however, this may not in fact correspond to the true location of this H atom.[17]

4.3.2. Single crystal X-ray structure determination of 6·2/3CH_2Cl_2. The asymmetric unit contains one molecule of the compound lying on a general position; a second half molecule with the CH_2–CH_2 bond spanning the inversion centre at [1/2, 1/2, 1/2]; and a wholly occupied molecule of CH_2Cl_2 occupying a general position. No disorder was detected during refinement, and no restraints were applied. All non-H atoms were refined anisotropically, while all H atoms were located in the difference map, but placed in calculated positions and refined using a riding model in the final least squares cycles.

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