# Two isomorphous transition metal complexes containing a protonated diaminopurine ligand: diaquabis(2,6-diamino-7H-purin-1-ium-κN⁹)bis-(homophthalato-κO)nickel(II) tetrahydrate and the cobalt(II) analogue

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The two isomorphous title compounds, $[M(C_5H_7N_6)_2(C_9H_6O_4)_2(H_2O)_2]\cdot 4H_2O$ or $M^{2+}(Hdap^+)_2(hpt^{2-})_2(H_2O)_2\cdot 4H_2O$ {where dap is 2,6-diaminopurine, $H_2$hpt is homophthalic acid [2-(2-carboxyphenyl)acetic acid] and $M$ is Ni$^{II}$ or Co$^{II}$}, consist of neutral $M^{2+}(Hdap^+)_2(hpt^{2-})_2(H_2O)_2$ monomers, where the $M^{II}$ cation lies on an inversion centre and its $MN_2O_4$ octahedral environment is defined by one N atom (from Hdap$^+$), two O atoms (from one hpt$^{2-}$ dianion and one water molecule) and their inversion images. The structures are unusual in that the Hdap$^+$ cation occurs in an uncommon protonated state (as 2,6-diamino-7H-purin-1-ium) and both ligands bind in an unprecedented monodentate fashion. The existence of a large number of donors and acceptors for hydrogen bonding, together with $\pi$–$\pi$ interactions, leads to a rather complex three-dimensional structure.

## Comment

2,6-Diaminopurine (dap) is a highly versatile entity for hydrogen bonding due to its many active sites which allow it to take part in extremely complex hydrogen-bonding networks, either as a donor or as an acceptor. We have recently reported (Atria *et al.*, 2010, 2011) some structures in which the molecule can occur either as a free base or as a cation. In all these cases, the (unbound) molecules or ions give rise to complex hydrogen-bonding schemes resulting from their intermolecular interactions. Moreover, in addition to its hydrogen-bonding capabilities, the molecule can also act as a mono-coordinated ligand binding to metal sites through an imidazole

N atom. The coordinating capabilities of dap, however, seem to be rather poor: only one compound with the molecule binding to a metal centre appears in the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002), in a Zn complex reported by Badura & Vahrenkamp (2002). In this Zn complex, the dap molecule is present with the imidazole ring completely deprotonated, behaving as a dap$^-$ anion. We report here two isomorphous transition metal complexes displaying a coordinated Hdap$^+$ cation, where the ligand binds to the metal centres in a similar mode but behaving as a singly protonated Hdap$^+$ cation. The complexes are completed by a homophthalate dianion (hpt$^{2-}$), giving the overall constitution $M^{2+}(Hdap^+)_2(hpt^{2-})_2(H_2O)_2\cdot 4H_2O$, where $M$ is Ni for (I) and Co for (II). These compounds are unusual in that they represent the first occurrence of the Hdap$^+$ cation acting in a monodentate N-coordinating role. Due to the fact that the Ni$^{II}$ and Co$^{II}$ structures are isomorphous, Figs. 1, 3 and 4 are restricted to compound (I) as representative of both.



(I) M = Ni
(II) M = Co
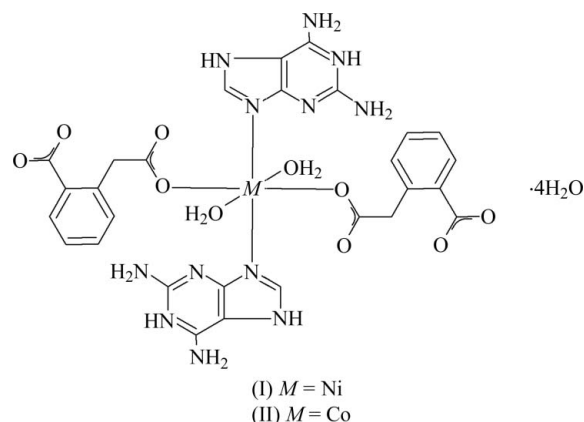
The structures consist of neutral monomers where the $M^{II}$ cations lie on inversion centres and the $MN_2O_4$ octahedral environment is defined by two O atoms (from one coordinated water molecule and one monodentate hpt$^{2-}$ dianion), one N atom (from one Hdap$^+$ cation) and their inversion images (Fig. 1). The resulting polyhedron is quite regular, with coordination distances in the range 2.0707 (14)–2.1116 (14) Å for Ni1 in (I) and 2.103 (2)–2.147 (2) Å for Co1 in (II). The intramolecular *cis* angles, in turn, differ from the ideal value of 90° by ±2.79 (5)° in (I) and ±2.14 (8)° in (II), while the *trans* angles are forced to be exactly 180° due to the symmetry constraints (Tables 1 and 3).

The hpt$^{2-}$ dianion binds in an unprecedented monodentate manner; all remaining examples in the literature of this ligand in metal complexes show it in a variety of chelating and/or bridging modes (Fig. 2), but never singly coordinated as in the present structure [structure '1b(*)' in Fig. 2]. Regarding its internal geometry, the carboxylate groups do not deviate significantly from their expected geometries; the COO$^-$ group is almost coplanar with the central benzyl core, while the CCOO$^-$ group is almost perpendicular, the out-of-plane angles being 5.5 (1)/81.7 (1) and 5.7 (1)/83.2 (1)° for (I)/(II), respectively. C—O distances are very sensitive to their invol-
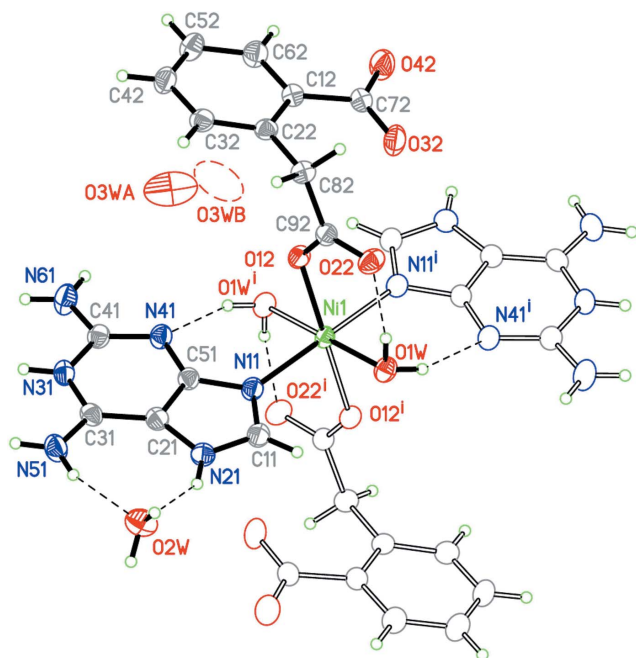
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**Figure 1**
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines. [Symmetry code: (i) −x + 1, −y + 1, −z + 1.]

vement in hydrogen bonding, and the longest C—O distances here correspond to O atoms triply involved in such interactions, *viz.* C92—O22. In this case, the softening is even more important than that introduced in C92—O12 by the coordination of atom O12 to the metal [C—O relative lengthening ∼1.5% in (I) and ∼2% in (II)].



Scheme 2
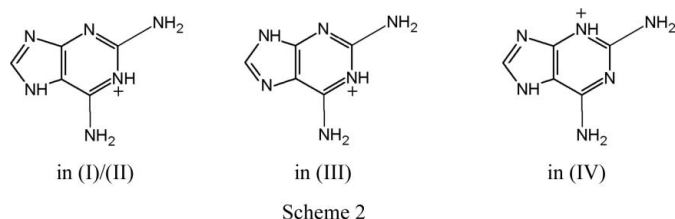
As already noted, the Hdap$^+$ group has not been frequently reported in the literature, and in the few known examples it occurs as an uncoordinated unit, so that the present binding mode can be regarded as novel. However, this is not the only point to make it unique. The only two structures so far reported containing such a cation are those of bis(2,6-diamino-9*H*-purin-1-ium) 2-(2-carboxylatophenyl)acetate heptahydrate, (III) (Atria *et al.*, 2010), and bis(2,6-diamino-1*H*-purin-3-ium) dicroconato-$\kappa^3O,O':O''$;$\kappa^3O:O',O''$-bis[tetraaqua(croconato-$\kappa^2O,O'$)neodymium(III)], (IV) (Atria *et al.*, 2011), so that all three Hdap$^+$ groups [appearing in (I)/(II), (III) and (IV)] are different in that protonation takes place at different N-atom sites, *viz.* at N2/N3 in (I)/(II) as 2,6-diamino-1*H*-purin-1-ium, at N2/N4 in (III) as 2,6-diamino-9*H*-purin-1-ium and at N1/N3 in (IV) as 2,6-diamino-1*H*-purin-3-ium. This form of tautomerism involving proton relocation is known as prototropy and has the effect of forcing a rearrangement in the

charge distribution, shown in Scheme 2 as different positioning of the single and double bonds around the rings. On the other hand, the metrics of the formal single and double bonds and the planarity of the ligand in (I) and (II) are comparable with those previously reported for (III) and (IV).

The intermolecular interactions are consequently the most distinctive features of both structures. The complex hydrogen-bonding scheme links the monomers together in an intricate fashion. Tables 2 and 4 present the main interactions of this sort, of various types and strengths. The first entry in each table corresponds to a hydrogen bond within the selected asymmetric unit, which helps to provide a tightly bound core around the $M^{II}$ cation (Fig. 3). Three N—H···O hydrogen bonds, having (N—H)$_{Hdap}$ groups as donors and O$_{hpt}$ atoms as acceptors, link the monomers together, defining chains parallel to [001] (Fig. 3), and these chains are in turn connected along [010] by two different $\pi$–$\pi$ contacts between aromatic rings, described in detail in Table 5 and shown in Fig. 3 as *A* and *B*. These contacts complete the formation of two-dimensional structures parallel to (100). Finally, the
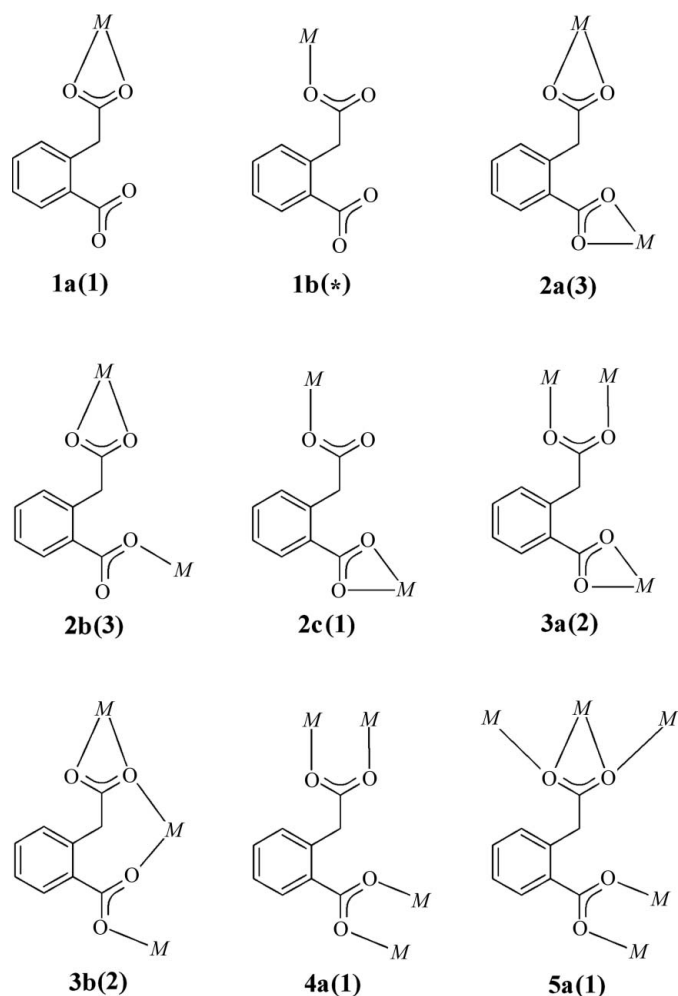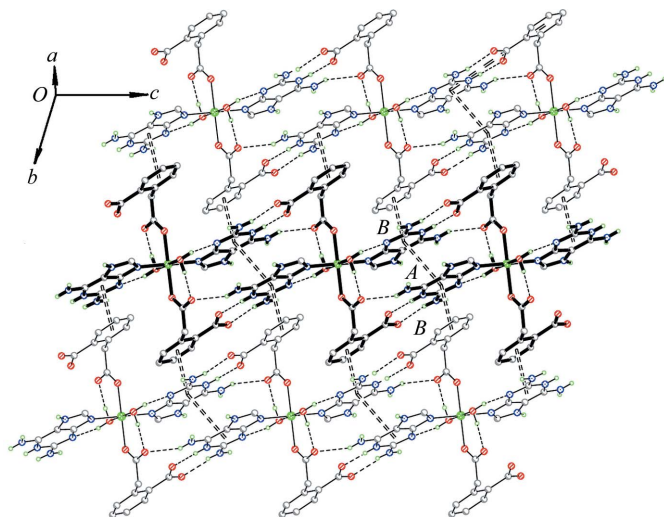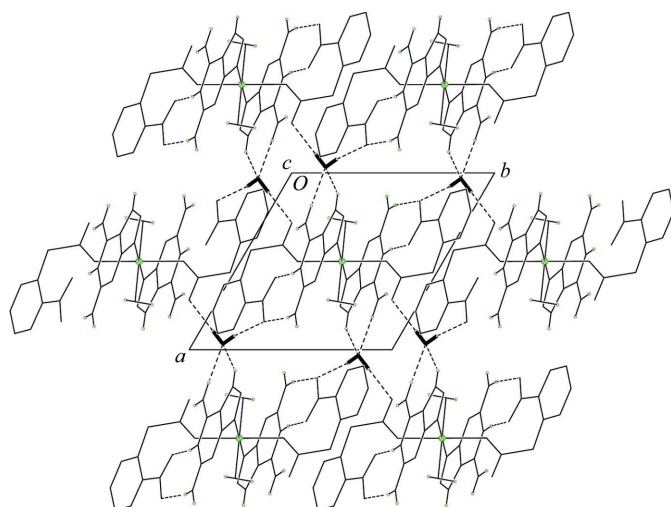


**Figure 2**
The binding modes shown by the homophthalate ligand. Explanation of the $\mu\kappa(n)$ naming: $\mu$ is the number of metal atoms coordinated/bridged by the ligand, $\kappa$ is the sequential label within the $\mu$ group and $n$ is the number of entries found in the CSD for the $\mu\kappa$ mode. Note: (*) this work.

**Figure 3**
A packing view of (I), parallel to the (100) plane, showing a clear view of the hydrogen-bonded chains running along [001] (one is highlighted for clarity). The chains are in turn interconnected by two types of $\pi$–$\pi$ contacts (*A* and *B*) to form two-dimensional structures parallel to (100).



**Figure 4**
A packing view of (I) in an [001] projection, at right angles to the plane shown in Fig. 3, showing the way in which the four hydrogen bonds involving water atom O2*W* link the planes together into a three-dimensional structure. H atoms involved in hydrogen bonding are drawn as small circles (green in the electronic version of the paper).

hydrogen bonds involving the uncoordinated water molecules link the planar arrays along [100] to form a three-dimensional structure. In this 'glueing' role, water molecule O2*W* stands out as a double donor as well as a double acceptor (Fig. 4; Tables 2 and 4, entries 6–9); the disordered water molecule O3*W* does not seem to be involved in any important interaction of this sort, the only detectable contact observed (Tables 2 and 4, entry 10) being quite long and thus very weak.

## Experimental

Complexes (I) and (II) were synthesized by adding an aqueous solution (80 ml) of $M$(acetate)$_2$·4H$_2$O (1 mmol) [$M$ = Ni for (I) and

Co for (II)] to an aqueous solution containing homophthalic acid (0.5 mmol) and NaOH (1 mmol). The resulting mixture was stirred for 5 min followed by the addition of a methanol solution (20 ml) of 2,6-diaminopurine (0.5 mmol). X-ray quality single crystals of (I) and (II) were obtained by slow evaporation of the filtered reaction mixture.

## Compound (I)

### Crystal data

| | |
|---|---|
| [Ni(C$_5$H$_7$N$_6$)$_2$(C$_9$H$_6$O$_4$)$_2$(H$_2$O)$_2$]·- 4H$_2$O | $\beta = 90.384\ (6)^\circ$ |
| $M_r = 825.41$ | $\gamma = 118.537\ (5)^\circ$ |
| Triclinic, $P\bar{1}$ | $V = 854.0\ (6)$ Å$^3$ |
| $a = 9.655\ (4)$ Å | $Z = 1$ |
| $b = 10.017\ (4)$ Å | Mo $K\alpha$ radiation |
| $c = 10.680\ (4)$ Å | $\mu = 0.66$ mm$^{-1}$ |
| $\alpha = 107.082\ (5)^\circ$ | $T = 150$ K |
| | $0.36 \times 0.32 \times 0.20$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 6856 measured reflections |
| Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2002) | 3607 independent reflections |
| | 3299 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.021$ |
| $T_{min} = 0.81$, $T_{max} = 0.88$ | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.097$ | |
| $S = 1.09$ | |
| 3607 reflections | $\Delta\rho_{max} = 0.52$ e Å$^{-3}$ |
| 302 parameters | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |
| 12 restraints | |

## Compound (II)

### Crystal data

| | |
|---|---|
| [Co(C$_5$H$_7$N$_6$)$_2$(C$_9$H$_6$O$_4$)$_2$(H$_2$O)$_2$]·- 4H$_2$O | $\beta = 90.371\ (4)^\circ$ |
| $M_r = 825.41$ | $\gamma = 118.019\ (3)^\circ$ |
| Triclinic, $P\bar{1}$ | $V = 857.3\ (3)$ Å$^3$ |
| $a = 9.651\ (2)$ Å | $Z = 1$ |
| $b = 10.045\ (2)$ Å | Mo $K\alpha$ radiation |
| $c = 10.661\ (2)$ Å | $\mu = 0.59$ mm$^{-1}$ |
| $\alpha = 107.400\ (4)^\circ$ | $T = 150$ K |
| | $0.28 \times 0.20 \times 0.16$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 7200 measured reflections |
| Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2002) | 3659 independent reflections |
| | 2634 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.034$ |
| $T_{min} = 0.81$, $T_{max} = 0.88$ | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.126$ | |
| $S = 1.00$ | |
| 3659 reflections | $\Delta\rho_{max} = 0.64$ e Å$^{-3}$ |
| 302 parameters | $\Delta\rho_{min} = -0.24$ e Å$^{-3}$ |
| 12 restraints | |

In both structures, uncoordinated water atom O3*W* appeared to be disordered over two sites; when the site-occupancy factors (SOFs) were refined independently, they converged to nearly complementary values, *viz.* 1.01 for (I) and 1.06 for (II). Thus, the condition

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## Table 1
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| Ni1—O1W | 2.0707 (14) | Ni1—O12 | 2.1116 (14) |
| Ni1—N11 | 2.1011 (15) | | |
| | | | |
| O1W—Ni1—N11 | 88.33 (6) | N11—Ni1—O12 | 90.00 (6) |
| O1W—Ni1—O12 | 92.79 (5) | | |

## Table 2
Hydrogen-bond geometry (Å, °) for (I).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1W—H1WA⋯O22 | 0.85 (3) | 1.82 (3) | 2.645 (2) | 163 (2) |
| O1W—H1WB⋯N41$^i$ | 0.85 (3) | 1.94 (3) | 2.733 (2) | 155 (3) |
| N31—H31⋯O32$^{ii}$ | 0.86 (3) | 1.69 (3) | 2.551 (2) | 168 (3) |
| N51—H51A⋯O22$^{ii}$ | 0.85 (3) | 2.23 (3) | 3.015 (2) | 151 (2) |
| N61—H61B⋯O42$^{ii}$ | 0.85 (3) | 2.01 (3) | 2.870 (2) | 177 (2) |
| O2W—H2WA⋯O22$^{iii}$ | 0.84 (3) | 1.91 (3) | 2.757 (2) | 173 (3) |
| O2W—H2WB⋯O42$^{iv}$ | 0.85 (3) | 1.93 (3) | 2.778 (2) | 170 (3) |
| N21—H21⋯O2W | 0.86 (3) | 2.02 (3) | 2.787 (2) | 148 (2) |
| N51—H51B⋯O2W | 0.85 (3) | 2.09 (3) | 2.930 (2) | 167 (2) |
| N61—H61A⋯O3WA | 0.85 (3) | 2.52 (3) | 3.277 (7) | 147 (2) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y, z+1$; (iii) $-x, -y, -z+1$; (iv) $x-1, y, z+1$.

## Table 3
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Co1—O1W | 2.103 (2) | Co1—N11 | 2.147 (2) |
| Co1—O12 | 2.1308 (19) | | |
| | | | |
| O1W—Co1—O12 | 92.14 (8) | O12—Co1—N11 | 89.27 (8) |
| O1W—Co1—N11 | 88.64 (8) | | |

## Table 4
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1W—H1WA⋯O22 | 0.85 (3) | 1.83 (3) | 2.647 (3) | 159 (4) |
| O1W—H1WB⋯N41$^i$ | 0.84 (3) | 1.92 (3) | 2.741 (3) | 161 (4) |
| N31—H31⋯O32$^{ii}$ | 0.86 (3) | 1.69 (3) | 2.552 (3) | 171 (4) |
| N51—H51A⋯O22$^{ii}$ | 0.86 (3) | 2.24 (3) | 3.011 (3) | 149 (3) |
| N61—H61B⋯O42$^{ii}$ | 0.84 (3) | 2.04 (3) | 2.877 (3) | 170 (3) |
| O2W—H2WA⋯O22$^{iii}$ | 0.85 (3) | 1.89 (3) | 2.748 (3) | 178 (3) |
| O2W—H2WB⋯O42$^{iv}$ | 0.85 (3) | 1.93 (3) | 2.775 (3) | 170 (4) |
| N21—H21⋯O2W | 0.85 (3) | 2.00 (3) | 2.785 (3) | 151 (3) |
| N51—H51B⋯O2W | 0.86 (3) | 2.08 (3) | 2.926 (4) | 166 (3) |
| N61—H61A⋯O3WA | 0.85 (3) | 2.51 (3) | 3.257 (9) | 147 (3) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y, z+1$; (iii) $-x, -y, -z+1$; (iv) $x-1, y, z+1$.

SOF(O3WA) + SOF(O3WB) = 1.0 was imposed. The restrained refinements of the SOFs converged to 0.808 (15):0.192 (15) for (I) and 0.776 (15):0.224 (14) for (II). In both cases, the minor component was refined isotropically. All the H atoms (except for those of the disordered O3W, which were not included in the model) were clearly located in difference maps but they were given different treatments. H atoms bonded to C atoms were repositioned at their expected locations and then treated as riding atoms, with C—H = 0.93–0.97 Å and $U_{iso}$(H) = $kU_{eq}$(parent), where $k$ = 1.2 or 1.5. H atoms bonded to O and N atoms were refined with restrained O/N—H distances of 0.85 (1) Å and free $U_{iso}$(H) values.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement and data reduction: *SAINT-NT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

## Table 5
$\pi$–$\pi$ contacts (Å, °) for (I) and (II).

$Cg1$ is the centroid of the N31/C31/C21/C51/N41/C41 ring and $Cg2$ is the centroid of the C12/C22/C32/C42/C52/C62 ring, CCD is the centre-to-centre distance, IPD is the mean interplanar distance, SA is the mean slippage angle and DA is the dihedral angle between rings (for details, see Janiak, 2000).

| Group 1/ Group 2 | Compound | CCD (Å) | DA (°) | SA (°) | IPD (Å) |
|---|---|---|---|---|---|
| $Cg1$⋯$Cg1^i$ | (I) | 3.630 (2) | 0.0 | 24.26 (1) | 3.311 (1) |
| | (II) | 3.576 (2) | 0.0 | 22.18 (1) | 3.311 (1) |
| $Cg1$⋯$Cg2^{ii}$ | (I) | 3.640 (2) | 9.94 (9) | 24 (3) | 3.32 (8) |
| | (II) | 3.643 (2) | 9.57 (14) | 24 (3) | 3.32 (9) |

Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $1-x, -y, 1-z$.

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