Two novel silver(I) coordination polymers: poly[(μ_2-2-aminopyrimidine-κ^2N^1:N^3)bis(μ_3-thiocyanato-κ^3S:S:S)disilver(I)] and poly[(2-amino-4,6-dimethylpyrimidine-κN)(μ_3-thiocyanato-κ^3N:S:S)silver(I)]

Geng-Geng Luo,[a] Di Sun,[a] Na Zhang,[a] Rong-Bin Huang[a]* and Lan-Sun Zheng[b]

[a]Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China, and [b]State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, People's Republic of China

Correspondence e-mail: rbhuang@xmu.edu.cn

2-Aminopyrimidine ($L1$) and 2-amino-4,6-dimethylpyrimidine ($L2$) have been used to create the two novel title complexes, $[Ag_2(NCS)_2(C_4H_5N_3)]_n$, (I), and $[Ag(NCS)(C_6H_9N_3)]_n$, (II). The structures of complexes (I) and (II) are mainly directed by the steric properties of the ligands. In (I), the $L1$ ligand is bisected by a twofold rotation axis running through the amine N atom and opposite C atoms of the pyrimidine ring. The thiocyanate anion adopts the rare μ_3-κ^3S coordination mode to link three tetrahedrally coordinated Ag^I ions into a two-dimensional honeycomb-like 6^3 net. The $L1$ ligands further extend the two-dimensional sheet to form a three-dimensional framework by bridging Ag^I ions in adjacent layers. In (II), with three formula units in the asymmetric unit, the $L2$ ligand bonds to a single Ag^I ion in a monodentate fashion, while the thiocyanate anions adopt a μ_3-κ^1N,κ^2S coordination mode to link the $AgL2$ subunits to form two-dimensional sheets. These layers are linked by N—H$\cdots$N hydrogen bonds between the noncoordinated amino H atoms and both thiocyanate and pyrimidine N atoms.

Comment

The rational design and construction of novel discrete and polymeric metal–organic complexes have been the subject of intense study in recent years, not only due to their structural and topological novelty of these complexes (Fujita *et al.*, 2004; Wang *et al.*, 2005, 2006), but also because of their potential application as functional materials in areas such as catalysis, molecular recognition, separation and nonlinear optics (Fujita *et al.*, 1994; Evans & Lin, 2002; Kasai *et al.*, 2000; Kitagawa *et*

al., 2004). The structure of metal–organic complexes is greatly influenced by many factors, such as the coordination geometry of the metal ion, the structure of the organic ligand, the solvent system, the counter-anion and the ratio of ligands to metal ions (Khlobystov *et al.*, 2003; Oxtoby & Champness, 2005). In addition, secondary forces such as hydrogen-bonding, π–π stacking and metal–metal interactions must also be considered (Blake *et al.*, 1999, 2000).
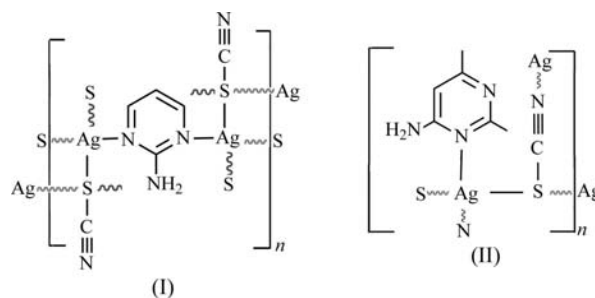

The thiocyanate anion is reported to show a rich variety of coordination modes through either the N or the S atom, or both, giving rise to linkage isomers or polymers. Silver(I) is a good candidate to be paired with thiocyanate as a soft acid favouring coordination to soft bases containing S and N atoms (Krautscheid *et al.*, 1998). Although the formation and crystal structures of complexes of AgSCN with various N-donor ligands such as substituted pyridine and polyamine ligands have been reported (Morpurgo *et al.*, 1984; Healy *et al.*, 1984, 1991; Ren *et al.*, 2001), complexes of AgSCN incorporating multidentate aminopyrimidine ligands have not appeared in the literature until now. Aminopyrimidine and its derivatives are considered interesting ligands from a supramolecular chemistry point of view due to the presence of one acceptor and two donor N atoms. This makes them well suited to developing polymeric metal–organic hybrid frameworks (Delgado *et al.*, 2003; Smith *et al.*, 1998; Chi *et al.*, 2006). In our recent investigations, 2-aminopyrimidine and its derivatives and/or other auxiliary ligands have been successfully used to construct a series of Ag^I complexes with structures spanning the full range from zero- to three-dimensional (Luo, Huang, Chen *et al.*, 2008; Luo, Huang, Zhang *et al.*, 2008; Luo *et al.*, 2009; Sun, Luo, Zhang *et al.*, 2009; Sun, Luo, Huang *et al.*, 2009). As a continuation of our work, we now report the two title novel silver(I) coordination polymers, (I) and (II), with different dimensionalities, based on the thiocyanate anion and the ligands 2-aminopyrimidine ($L1$) or 2-amino-4,6-dimethylpyrimidine ($L2$).

The crystal structure of complex (I) consists of a silver(I) thiocyanate–$L1$ adduct in a 2:1 stoichiometry (Fig. 1). The $L1$ ligand sits on a special position with the twofold rotation axis running through atoms N1, C1 and C3 of the pyrimidine ring. Each Ag^I ion is coordinated to one pyrimidine N atom of $L1$ and three different thiocyanate S atoms, resulting in a distorted tetrahedral coordination geometry, with one S—Ag—N angle opened up to 133.35 (11)° and the remaining angles in the range 93.39 (12)–114.81 (11)° (Table 1). The Ag—S bond lengths fall in the range 2.5832 (15)–2.8851 (16) Å, comparable with those found in other AgSCN-
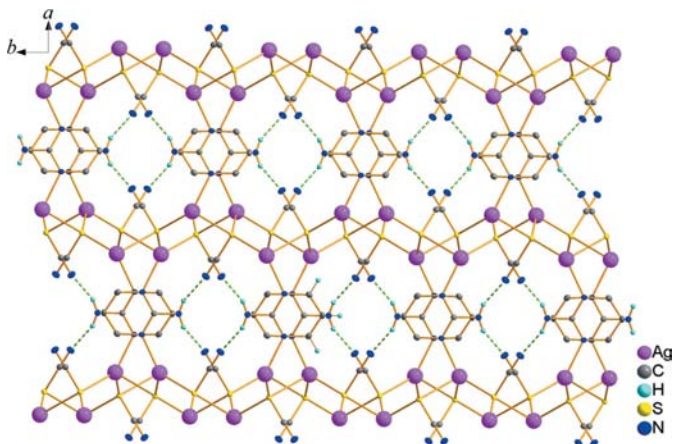
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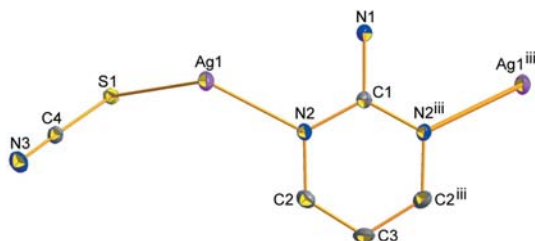
Figure 1
The asymmetric unit of (I), together with a symmetry-generated portion of 2-aminopyrimidine and an adjacent Ag atom, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [Symmetry code: (iii) $1 - x, y, \frac{1}{2} - z$.]
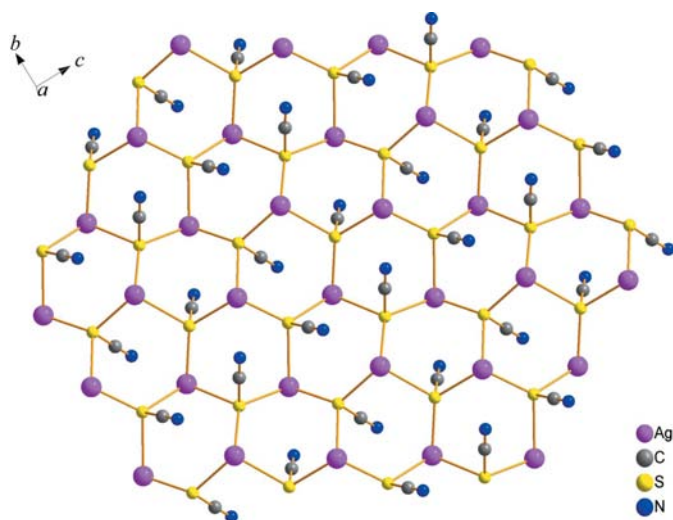
Figure 2
The two-dimensional honeycomb-like net bridged by thiocyanate anions in (I), viewed along the a axis.

Figure 3
The three-dimensional framework of (I), with the N—H···N hydrogen bonds shown as dashed lines.

containing complexes (Corradi Bonamartini *et al.*, 1987). Each thiocyanate anion adopts a μ_3-$\kappa^3 S$ coordination mode, linking three silver(I) ions to form an Ag_3S_3 boat-like six-membered ring (Fig. 2). This repeat unit shares the Ag–S edges, extending the structure into a two-dimensional honeycomb-like 6^3 net parallel to the *bc* plane. To the best of our knowledge, (I) is the first complex containing a thiocyanate anion with a μ_3-$\kappa^3 S$ coordination mode, and the characteristic IR spectroscopic absorption for a μ_3-$\kappa^3 S$ thiocyanate anion occurs at ~2130 cm^{-1}. The coordination mode of the thiocyanate anion in (I) obviously follows Pearson's principle of hard and soft Lewis acids and bases (HSAB), according to which the 'soft' Ag^I ions should bind preferentially to the 'softer' S atoms of the thiocyanate groups (Pearson, 1963). Adjacent two-dimensional nets stacked along the *a* axis are linked by *L*1 ligands with μ_2-*N*:*N'* coordination modes to create a three-dimensional framework (Fig. 3). Since the thiocyanate anions use only their S atoms to bind to the silver(I) atoms, the uncoordinated N atoms are available to act as acceptors to form hydrogen bonds with the amino groups of *L*1, which further stabilizes the resulting framework (Table 2 and Fig. 3).

Complex (II) contains three crystallographically independent silver(I) atoms and the stoichiometry for the silver(I) thiocyanate–*L*2 adduct is 1:1 (Fig. 4). Each Ag^I atom is coordinated by one N atom from *L*2, and two S atoms and one N atom from each of three different thiocyanate anions, resulting in a tetrahedral coordination geometry with bond angles ranging from 97.85 (15) to 135.47 (14)° (Table 3). Each thiocyanate anion adopts a μ_3-$\kappa^1 N$, $\kappa^2 S$ coordination mode to link three Ag^I atoms to form a saddle-like ten-membered ring (Fig. 5), and these repeat units are fused together to form a wave-shaped two-dimensional net in the *ab* plane. The IR spectroscopic absorption in the range 2100–2107 cm^{-1} indicates the existence of bridging μ_3-$\kappa^1 N,\kappa^2 S$ thiocyanate anions in (II) (Shen & Xu, 2001). The *L*2 ligands only adopt a monodentate coordination mode and thus do not extend the two-dimensional network to a higher dimension as in (I), which may be due to the more intense steric effects in *L*2 than in *L*1. Adjacent nets are joined together to form a three-dimensional framework by N—H···N hydrogen bonds from the amino groups to the noncoordinated pyrimidine N atoms of the *L*2 ligands and the coordinated N atoms of the thiocyanate anions (Fig. 6).

In summary, we have successfully assembled two different silver(I) coordination polymers from 2-aminopyrimidine derivatives (ligands *L*1 and *L*2) and AgSCN. The structures of the two title complexes are governed by the nature of the aminopyrimidine derivatives and the different coordination modes of the thiocyanate anions. Recently, we found that trigonal nitrate as a chelating counter-anion reacts with Ag^I
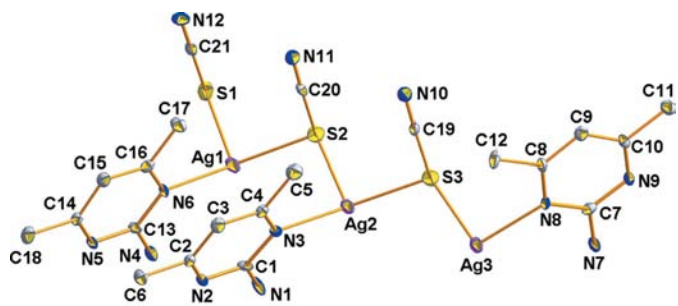
Figure 4
The asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted.
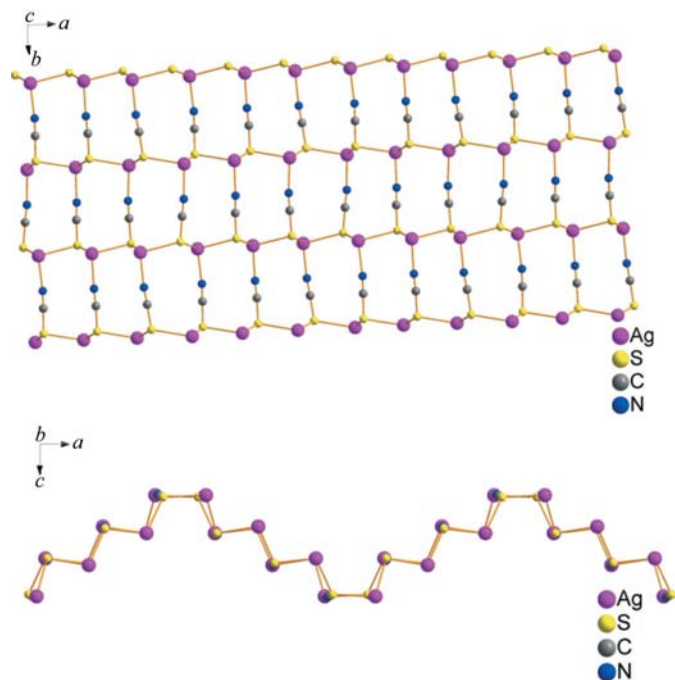
Figure 5
The two-dimensional saddle-like net in (II), viewed along two different axes.
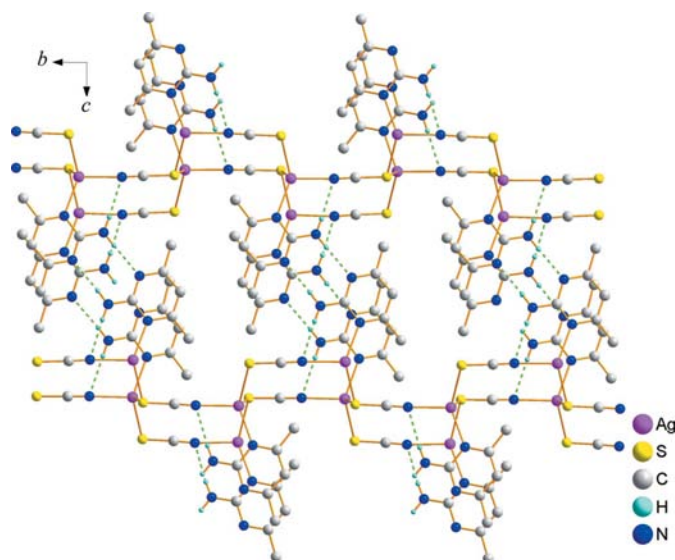
Figure 6
The three-dimensional framework of (II), with the hydrogen bonds shown as dashed lines.

and $L1$ to give $[Ag(L1)(NO_3)]_n$ in the form of a one-dimensional zigzag chain structure (Luo, Huang, Zhang *et al.*, 2008). By contrast, in (I) the linear thiocyanate anions possess two kinds of potential terminal coordination atoms and the 'softer' μ_3-S atoms link the soft Ag^I atoms to form a two-dimensional honeycomb structure. When trigonal nitrate and tetrahedral perchlorate counter-anions were chosen to react with Ag^I and $L2$, the results were the tetranuclear $[Ag_4(L2)_6(NO_3)_4]$ and dinuclear $[Ag_2(L2)_4(ClO_4)_2]$ zero-dimensional molecular structures, respectively (Luo, Huang, Chen *et al.*, 2008; Luo,

Huang, Zhang *et al.*, 2008). In (II), thiocyanate anions with two different coordinated atoms link the Ag atoms to form a two-dimensional rectangular net structure. Thus, it is evident that the thiocyanate anion promotes higher dimensionalities in these systems.

Experimental

All reagents and solvents were commercially available and were used as received. For (I), AgSCN (0.5 mmol, 83 mg) was dissolved in a saturated aqueous solution of KSCN (5 ml), and then $L1$ (0.5 mmol, 48 mg) in acetonitrile (5 ml) was carefully layered on top. The whole reaction system was kept in the dark at room temperature, and colourless block-shaped crystals of (I) were obtained after 3 d. The crystals were filtered off, washed with distilled water and acetonitrile, and left to dry in the dark at room temperature (yield 66 mg, 62%). Analysis calculated for $C_6H_4Ag_2N_5S_2$: C 16.92, H 0.95, N 16.44%; found: C 16.99, H 1.05, N 16.36%. IR (KBr, ν, cm^{-1}): 3450 (*w*), 3339(*w*), 2130 (*s*), 1612 (*s*), 1580 (*s*), 1463 (*s*), 1423 (*w*), 1358 (*m*), 1312 (*w*), 1222 (*m*), 1165 (*w*), 1163 (*w*), 1100 (*w*), 1064 (*w*), 965 (*w*), 792 (*m*), 777 (*s*), 739 (*m*), 662 (*m*), 634 (*w*), 412 (*w*), 409 (*w*). The synthesis of (II) was similar to that of (I), but with $L2$ (0.5 mol, 65 mg) in place of $L1$ (yield 75 mg, 52%). Crystals were grown using the same method as for (I). Analysis calculated for $C_7H_9AgN_4S$: C 29.08, H 3.14, N 19.38%; found: C 29.12, H 3.08, N 19.45%. IR (KBr, ν, cm^{-1}): 3396 (*w*), 3302 (*w*), 2107 (*s*), 2100 (*s*), 1623 (*s*), 1582 (*s*), 1465 (*s*), 1427 (*w*), 1360 (*m*), 1324 (*w*), 1225 (*m*), 1168 (*w*), 1160 (*w*), 1101 (*w*), 1006 (*w*), 828 (*m*), 822 (*w*), 789 (*m*), 782 (*m*), 757 (*w*), 747 (*w*), 732 (*w*), 693 (*w*), 675 (*w*), 666 (*m*), 619 (*w*), 474 (*w*), 434 (*w*), 452 (*w*).

Compound (I)

Crystal data

$[Ag_2(NCS)_2(C_4H_5N_3)]$	$V = 1059.1$ (6) Å^3
$M_r = 427.01$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 17.719$ (6) Å	$\mu = 4.06$ mm^{-1}
$b = 8.159$ (3) Å	$T = 298$ K
$c = 7.326$ (2) Å	$0.10 \times 0.05 \times 0.05$ mm

Data collection

Oxford Gemini S Ultra diffractometer	4766 measured reflections
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009)	1034 independent reflections
	992 reflections with $I > 2\sigma(I)$
$T_{min} = 0.687$, $T_{max} = 0.823$	$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	71 parameters
$wR(F^2) = 0.104$	H-atom parameters constrained
$S = 1.22$	$\Delta\rho_{max} = 0.95$ e Å^{-3}
1034 reflections	$\Delta\rho_{min} = -0.61$ e Å^{-3}

Compound (II)

Crystal data

$[Ag(NCS)(C_6H_9N_3)]$	$V = 5713$ (2) Å^3
$M_r = 289.11$	$Z = 24$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 20.955$ (4) Å	$\mu = 2.29$ mm^{-1}
$b = 11.282$ (2) Å	$T = 173$ K
$c = 24.166$ (5) Å	$0.13 \times 0.10 \times 0.08$ mm

metal-organic compounds

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

Ag1—N2	2.303 (4)	Ag1—S1	2.6252 (16)
Ag1—S1^i	2.5832 (15)	Ag1—S1^{ii}	2.8851 (16)
N2—Ag1—S1^i	133.35 (11)	S1^i—Ag1—S1	108.83 (3)
N2—Ag1—S1	114.81 (11)	S1^i—Ag1—S1^{ii}	96.44 (4)
N2—Ag1—S1^{ii}	93.39 (12)	S1—Ag1—S1^{ii}	97.74 (4)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, -y, z + \frac{1}{2}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$N3^{iii}	0.86	2.26	3.042 (6)	151

Symmetry code: (iii) $x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

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

Ag1—N6	2.289 (5)	Ag2—S2	2.6485 (19)
Ag1—N11^i	2.296 (6)	Ag2—S3	2.5176 (17)
Ag1—S1	2.667 (2)	Ag3—N8	2.286 (5)
Ag1—S2	2.5269 (18)	Ag3—N10^{ii}	2.295 (6)
Ag2—N12^i	2.303 (6)	Ag3—S1^{iii}	2.5075 (17)
Ag2—N3	2.307 (5)	Ag3—S3	2.7126 (19)
N6—Ag1—N11^i	109.5 (2)	N12^i—Ag2—S2	97.85 (15)
N6—Ag1—S2	130.90 (14)	N8—Ag3—N10^{ii}	109.0 (2)
N6—Ag1—S1	107.85 (13)	N8—Ag3—S1^{iii}	135.47 (14)
N11^i—Ag1—S1	100.49 (16)	N8—Ag3—S3	102.29 (13)
N11^i—Ag1—S2	102.86 (15)	N10^{ii}—Ag3—S1^{iii}	105.26 (15)
N3—Ag2—N12^i	108.61 (19)	N10^{ii}—Ag3—S3	98.72 (16)
N3—Ag2—S2	102.64 (13)	S1—Ag1—S2	101.20 (6)
N3—Ag2—S3	132.61 (15)	S1^{iii}—Ag3—S3	99.63 (6)
N12^i—Ag2—S3	104.82 (15)	S2—Ag2—S3	105.00 (6)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$N9^{iv}	0.88	2.17	3.025 (7)	165
N1—H1$B\cdots$N12^i	0.88	2.26	3.133 (8)	169
N4—H4$A\cdots$N5^v	0.88	2.11	2.989 (7)	178
N4—H4$B\cdots$N11^i	0.88	2.25	3.125 (8)	175
N7—H7$A\cdots$N10^{ii}	0.88	2.24	3.110 (8)	168
N7—H7$B\cdots$N2^{vi}	0.88	2.13	2.993 (7)	165

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z + 2$; (vi) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

Data collection

Oxford Gemini S Ultra diffractometer	29723 measured reflections
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009) $T_{min} = 0.755$, $T_{max} = 0.838$	5603 independent reflections 3440 reflections with $I > 2\sigma(I)$ $R_{int} = 0.115$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	358 parameters
$wR(F^2) = 0.125$	H-atom parameters constrained
$S = 0.90$	$\Delta\rho_{max} = 1.39$ e Å^{-3}
5603 reflections	$\Delta\rho_{min} = -0.72$ e Å^{-3}

For both compounds, all H atoms were refined using a riding model, with C—H = 0.95 (aromatic) or 0.98 Å (CH$_3$) and N—H = 0.86 [for (I)] or 0.88 Å [for (II)], with U_{iso}(H) = 1.2U_{eq}(C or N).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2009).

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