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‡ These authors contributed equally to this work.

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Structural adaptability and hydrogen bonding in a dissymmetric pyrimidine thioether ligand

Kaycee Anoliefo,^{a‡} Kaitlyn Brown,^{a‡} Lana K. Hiscock,^b Paul D. Boyle^c and Louise N. Dawe^{a*}

^aDepartment of Chemistry and Biochemistry, Wilfrid Laurier University, 75 University Ave. W., Waterloo, Ontario, N2L 3C5, Canada, ^bDepartment of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, M3J 1P3, Canada, and ^cDepartment of Chemistry X-ray Facility, University of Western Ontario, 1151 Richmond Street North, London, Ontario, N6A 5B7, Canada. *Correspondence e-mail: ldawe@wlu.ca

Dissymmetric ligands have garnered interest due to their ability to simultaneously coordinate to multiple different acceptors. Herein, we report the synthesis of a dissymmetric thioether *N,N'*-bidentate ligand, namely, 2-[(6-chloropyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine ($C_8H_7ClN_6S$, **L1**), along with its hydrated form ($C_8H_7ClN_6S \cdot H_2O$). In addition, we describe the structure of a nitrate salt of the protonated ligand [4,6-diamino-2-[(6-chloropyrimidin-4-yl)sulfanyl]pyrimidin-1-ium nitrate, $C_8H_8ClN_6S^+ \cdot NO_3^-$] and a cobalt(II) complex of **L1** (dichlorido[2-[(6-chloropyrimidin-4-yl- κN^3)sulfanyl]pyrimidine-4,6-diamine- κN^3]cobalt(II), $[CoCl_2(C_8H_7ClN_6S)]$). The structures of all four compounds were determined by single-crystal X-ray diffraction and Hirshfeld surface analyses were performed. These analyses reveal unengaged hydrogen-bond donors and acceptors in both the neutral ligand and its water solvate, while protonation or metal coordination induces a conformational change that enables full engagement of hydrogen-bond donors. These structural insights have implications for the molecular design of ligands in ion-sensing applications.

1. Introduction

Our group is interested in the structure, properties and applications of multifunctional ligands capable of coordinating to metal cations and participating in intermolecular interactions with anions. We are particularly motivated by a knowledge gap related to the directionality of weak intermolecular forces, which challenges the rational design of functional coordination complexes (Molina *et al.*, 2017; Chakrabarty *et al.*, 2011; Desiraju, 2007). Among the systems of interest are dissymmetric ligands, which have garnered attention for their capacity to simultaneously coordinate different metal cations and to mediate a range of noncovalent interactions (Liu *et al.*, 2018; Yang *et al.*, 2016). These ligands, and their resulting coordination complexes, have demonstrated applications across catalysis, magnetism and the design of novel supramolecular architectures (Adilkhanova *et al.*, 2023; Worrell *et al.*, 2023; Xu *et al.*, 2022).

Recent interest has focused on dissymmetrical Schiff base ligands which can support various metal-to-ligand coordination modes and stoichiometries (Costes *et al.*, 2020; Liu *et al.*, 2018; Dehghani-Firouzabadi *et al.*, 2016). Examples include those with *N,N',S*-donor sets, which can act as *N,S*-bidentate or *N,N',S*-tridentate ligands and form stable four-, five- or six-coordinated complexes (Dehghani-Firouzabadi *et al.*, 2017, 2020) (Fig. 1).

Strategic ligand design in coordination chemistry can be used to promote direct interaction between cationic metal

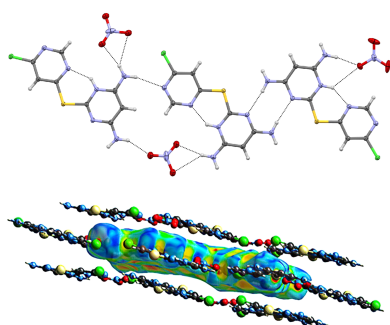


Table 1

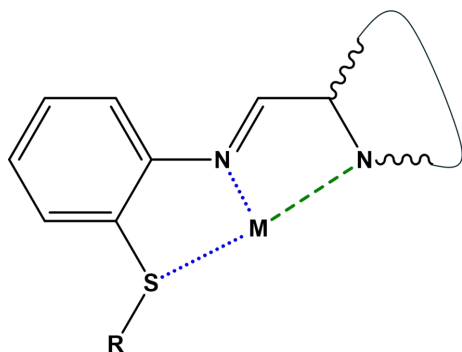
Experimental details.

Experiments were carried out at 110 K with Mo $K\alpha$ radiation using a Bruker APEXII CCD diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	L1	L1·H ₂ O	[L1+H][NO ₃]	L1CoCl ₂
Crystal data				
Chemical formula	C ₈ H ₇ ClN ₆ S	C ₈ H ₇ ClN ₆ S·H ₂ O	C ₈ H ₈ ClN ₆ S ⁺ ·NO ₃ [−]	[CoCl ₂ (C ₈ H ₇ ClN ₆ S)]
M_r	254.71	272.72	317.72	384.54
Crystal system, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	13.5864 (6), 6.8262 (3), 11.6234 (5)	3.8868 (15), 14.652 (6), 19.154 (7)	19.541 (8), 18.048 (9), 6.851 (4)	7.763 (2), 24.510 (9), 7.152 (3)
α, β, γ (°)	90, 90, 90	90, 90.147 (7), 90	90, 92.765 (11), 90	90, 97.464 (4), 90
V (Å ³)	1077.99 (8)	1090.8 (8)	2413 (2)	1349.4 (9)
Z	4	4	8	4
μ (mm ^{−1})	0.53	0.54	0.51	2.01
Crystal size (mm)	0.19 × 0.17 × 0.08	0.28 × 0.13 × 0.13	0.25 × 0.07 × 0.06	0.39 × 0.16 × 0.05
Data collection				
Absorption correction	Multi-scan (SADABS2016; Bruker, 2016)	Multi-scan (SADABS2016; Bruker, 2016)	Multi-scan (SADABS2016; Bruker, 2016)	Empirical (using intensity measurements) (TWINABS2012; Bruker, 2012)
$T_{\min}, T_{\max}$	0.688, 0.747	0.685, 0.749	0.674, 0.746	0.532, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	87768, 5788, 5131	128142, 8646, 6849	90727, 6784, 4861	71073, 2659, 2324
R_{int}	0.057	0.051	0.090	0.067
($\sin \theta/\lambda$) _{max} (Å ^{−1})	0.863	0.981	0.696	0.618
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.075, 1.04	0.030, 0.088, 1.04	0.043, 0.105, 1.03	0.044, 0.087, 1.15
No. of reflections	5788	8646	6784	2659
No. of parameters	161	178	399	184
No. of restraints	7	7	44	6
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.41, −0.26	0.64, −0.36	0.88, −0.92	0.69, −0.43
Absolute structure	Flack x determined using 2256 quotients [$(I^+) - (I^-) / [(I^+) + (I^-)]$] (Parsons <i>et al.</i> , 2013)	—	—	—
Absolute structure parameter	0.02 (2)	—	—	—

Computer programs: APEX2 (Bruker, 2018), SAINT (Bruker, 2018), SHELXT2018 (Sheldrick, 2015a), SHELXL2019 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

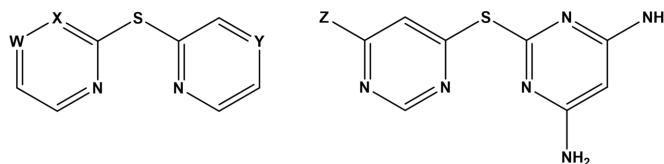
centres and target anions. Such interactions occur through primary-sphere coordination, wherein the anion occupies a metal coordination site (Mercer & Loeb, 2010). However, achieving selectivity and stability under competitive conditions, especially in polar solvents, often requires second-

**Figure 1**

Previously reported N,N' - S -donor ligands capable of N,S -bidentate (blue) or N,N',S -tridentate (blue and green) metal coordination [based on the work of Dehghani-Firouzabadi *et al.* (2016, 2017, 2020)]. The presence of coligands at the metal site, M , results in four-, five- or six-coordinated complexes.

sphere coordination. In this approach, the anion binds to a ligand that is already coordinated to a metal centre, *via* hydrogen bonding or electrostatic interactions (Hiscock *et al.*, 2019; Moyaert *et al.*, 2018; Mercer & Loeb, 2010). These interactions can be perturbed or promoted by solvent effects, as solvent molecules may act as hydrogen-bond acceptors or coordinate directly to the metal centre, thereby altering the binding environment (Zhao *et al.*, 2019; Robertson *et al.*, 2017).

Second-sphere interactions are especially relevant to supramolecular assembly strategies. For example, Teles *et al.* (2006) demonstrated the use of thioether-based N,N' -biden-

**Figure 2**

(Left) Previously reported thioether ligands with $W = X = Y = \text{CH}$ (Teles *et al.*, 2006); $X = Y = \text{N}$, $W = \text{CH}$; and $W = Y = \text{N}$, $X = \text{CH}$ (Fresta *et al.*, 2022). (Right) N,N' -Bidentate ligands derived from 4,6-dichloropyrimidine, with $Z = \text{N}(\text{CH}_3)_2$ (Moyaert *et al.*, 2017) or Cl (**L1**; this work).

tate spacer ligands in the self-assembly of supramolecular arrays, relying on directional noncovalent interactions (Fig. 2). Similarly, the design of luminescent materials often exploits these principles (Pashaei *et al.*, 2019); for example, Fresta *et al.* (2022) reported red-emitting copper(I) complexes incorporating pyrimidinyl ligands (Fig. 2) for use in white light-emitting electrochemical cells, where secondary interactions contribute to emissive properties and molecular packing.

In the present work, we examine a dissymmetric thioether *N,N'*-bidentate ligand derived from 4,6-dichloropyrimidine, which reflects this design logic, and builds on our previously reported work (Moyaert *et al.*, 2017). Herein, we report the synthesis and solid-state characterization of 2-[(6-chloropyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine (**L1**), its hydrated form (**L1**·H₂O), its protonated nitrate salt [**L1**+H][NO₃] and its cobalt(II) complex (**L1**CoCl₂). Single-crystal X-ray diffraction studies, supported by Hirshfeld surface analysis, were undertaken to assess the primary and secondary coordination features of these structures. These results lay the groundwork for future studies on ligand modification and complexation, including the introduction of additional functionality at the chloro-substituted pyrimidine ring to support extended coordination motifs.

2. Experimental

2.1. General procedures

The ¹H NMR spectrum was recorded on an Agilent Technologies Varian Unity Inova 400 MHz NMR spectrometer. Chemical shifts are reported in δ scale using the residual ¹H solvent peak (DMSO-*d*₆, δ = 2.50 ppm) as reference. 4,6-Dichloropyrimidine (TCI) and 4,6-diaminopyrimidine-2-thiol (Merck) were used as purchased. All other reagents and starting materials were purchased from Sigma-Aldrich and used as purchased. Melting points were determined on a Mel-Temp electrothermal melting-point apparatus and are uncorrected. Single crystals were selected and collected on a Bruker APEXII CCD diffractometer at Western University, London, ON, Canada. Crystals were kept at 110 (2) K during data collection. Using OLEX2 (Dolomanov *et al.*, 2009), the structures were solved with the SHELXT

(Sheldrick, 2015a) structure solution program using direct methods and refined with the SHELXL (Sheldrick, 2015b) refinement package using least-squares minimization.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms, except where noted otherwise, were placed geometrically (C–H = 0.95 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom. All non-H atoms were refined anisotropically. For **L1**, **L1**·H₂O and [**L1**+H][NO₃], amine H atoms (bound to N5 and N6 in all structures, and additionally to N11 and N12 in [**L1**+H][NO₃]) were located in difference maps, refined positionally with similarity restraints (SHELXL SADI) and treated isotropically, while in **L1**CoCl₂, these H atoms were refined with an isotropic displacement fixed at 1.5 times that of the carrier atom. For **L1**·H₂O, the H atoms on the O atom (*i.e.* water atom O1) were treated similarly. In [**L1**+H][NO₃], $Z' = 2$, and one disordered nitrate anion was present with occupancies of 0.672 (3) and 0.328 (3). The O atoms of this group were constrained to have identical anisotropic displacements (SHELXL EADP). For **L1**CoCl₂, a minor second twin domain (BASF < 8%) was identified. Including this domain (SHELXL HKLF5) resulted in higher refinement statistics and a model that did not converge satisfactorily. Therefore, the second domain was excluded from the final refinement, which was performed using the single-domain HKLF4 reflection file.

2.3. Synthesis of L1

4,6-Dichloropyrimidine (2.00 g, 13.4 mmol, 1.00 equiv.) was added to a 250 ml round-bottomed flask containing 100 ml of ethanol. Triethylamine (1.87 ml, 13.5 mmol, 1.00 equiv.) was added *via* syringe and the mixture was stirred at room temperature for 15 min, resulting in a clear colourless solution. Subsequently, 20 ml of dimethylformamide (DMF) and 1.908 g of 4,6-diaminopyrimidine-2-thiol (13.5 mmol, 1.00 equiv.) were added, yielding an opaque white solution. The reaction mixture was heated under reflux for 48 h, resulting in a clear yellow solution with a white precipitate upon cooling to room temperature. Deionized water (150 ml) was added, dissolving the precipitate. The solution was transferred to a 500 ml round-bottomed flask and concentrated by rotary evaporation to approximately 100 ml. The residue was extracted three times with dichloromethane using a 500 ml separatory funnel. The combined organic layers were dried over anhydrous MgSO₄, filtered by gravity and concentrated by rotary evaporation to afford a dark red–yellow oil. After cooling to room temperature, 50 ml of cold deionized water were added and the mixture was stirred in an ice bath for 24 h. The resulting white solid was collected by suction filtration and dried to give the product as a white solid (yield: 1.365 g, 55.8%). ¹H NMR (400 MHz, DMSO): δ 8.79 (s, 1H), 8.46 (s, 1H), 6.45 (s, 4H), 5.26 (s, 1H). IR (ATR, cm^{−1}): 3610, 3441, 3309 (NH₂); 751 (C–S); 1637 (C=N); 806 (C–Cl). HRMS (TOF) m/z : [$M + H$] + Calcd for C₈H₇ClN₆S 255.02142; found 255.02171. The reaction scheme is presented in Scheme 1.

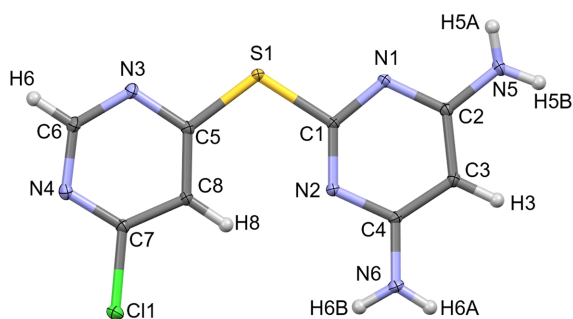


Figure 3

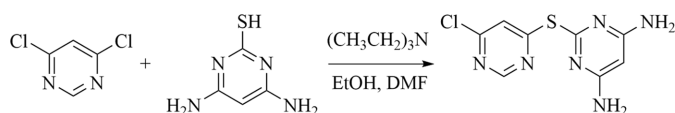
The asymmetric unit of **L1**, drawn with 50% probability displacement ellipsoids for the non-H atoms.

Table 2

Selected hydrogen bonds (Å, °) described by primary associated graph-set notation.

<i>D</i>	H	<i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>	Associated graph-set motif
L1							
N5	H5 <i>B</i>	N4 ⁱ	0.84 (2)	2.21 (2)	3.023 (2)	162 (3)	<i>C</i> (10)
N6	H6 <i>A</i>	N1 ⁱⁱ	0.81 (2)	2.29 (2)	3.0215 (19)	150 (2)	<i>C</i> (6)
N6	H6 <i>B</i>	N3 ⁱⁱⁱ	0.853 (19)	2.33 (2)	3.087 (2)	148 (2)	<i>C</i> (8)
L1·H₂O							
N6	H6 <i>A</i>	O1 ^{iv}	0.873 (11)	2.191 (11)	3.0625 (13)	176.3 (13)	<i>D</i> (2)
N6	H6 <i>B</i>	O1 ^v	0.854 (11)	2.217 (11)	3.0472 (12)	164.2 (13)	<i>D</i> (2)
N5	H5 <i>A</i>	N4 ^{vi}	0.855 (11)	2.588 (12)	3.3899 (12)	156.7 (12)	<i>C</i> (10)
N5	H5 <i>B</i>	N1 ^{vii}	0.848 (11)	2.282 (12)	3.1182 (14)	169.0 (13)	<i>R</i> ₂ ² (8)
[L1+H][NO₃]							
N1	H1	N3	0.88 (2)	1.93 (3)	2.681 (3)	142 (3)	<i>S</i> (6)
N5	H5 <i>A</i>	N4 ^{viii}	0.837 (16)	2.319 (17)	3.134 (3)	165 (2)	<i>C</i> (10)
N5	H5 <i>B</i>	O1	0.834 (16)	1.966 (17)	2.789 (3)	169 (3)	<i>D</i> (2)
N6	H6 <i>A</i>	O3 ^{viii}	0.844 (16)	2.000 (16)	2.843 (3)	176 (3)	<i>D</i> (2)
N6	H6 <i>B</i>	N8	0.844 (16)	2.142 (17)	2.983 (3)	174 (3)	<i>R</i> ₂ ² (8)
N7	H7	N9	0.89 (2)	1.92 (3)	2.675 (3)	142 (3)	<i>S</i> (6)
N11	H11 <i>A</i>	O4	0.838 (16)	2.112 (18)	2.936 (4)	167 (3)	<i>D</i> (2)
N11	H11 <i>A</i>	O5 <i>A</i>	0.838 (16)	1.807 (19)	2.630 (8)	167 (3)	<i>D</i> (2)
N11	H11 <i>B</i>	N10 ^{ix}	0.845 (16)	2.328 (18)	3.150 (3)	164 (3)	<i>D</i> (2)
N12	H12 <i>A</i>	N2	0.841 (15)	2.203 (16)	3.040 (3)	174 (2)	<i>R</i> ₂ ² (8)
N12	H12 <i>B</i>	O6 ^{ix}	0.842 (16)	2.10 (2)	2.872 (4)	152 (3)	<i>D</i> (2)
N12	H12 <i>B</i>	O4 <i>A</i> ^{ix}	0.842 (16)	1.922 (18)	2.763 (6)	175 (3)	<i>D</i> (2)
L1CoCl₂							
N5	H5 <i>A</i>	Cl2 ^x	0.81 (3)	2.63 (3)	3.385 (4)	156 (5)	<i>C</i> (10)
N5	H5 <i>B</i>	Cl3	0.81 (3)	2.53 (3)	3.320 (4)	163 (5)	<i>S</i> (6)
N6	H6 <i>A</i>	Cl2 ^{xi}	0.81 (3)	2.61 (3)	3.400 (4)	164 (5)	<i>C</i> (10)
N6	H6 <i>B</i>	N2 ^{xii}	0.81 (3)	2.29 (3)	3.096 (5)	174 (5)	<i>R</i> ₂ ² (8)

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



Scheme 1

2.4. Synthesis of L1·H₂O and [L1+H][NO₃]

Unsuccessful attempts to synthesize Lewis acid/base complexes using a methodology consistent with that employed for **L1CoCl₂** (*vide infra*), but with a mixed solvent system of acetonitrile, ethyl acetate and water, resulted instead in the formation of crystals of the hydrate of **L1**, **L1·H₂O**, when MnSO₄·4H₂O was used, and the nitrate salt of the protonated ligand, **[L1+H][NO₃]**, when Ga(NO₃)₃·H₂O was used. In the presence of water and protic solvents, protonation or solvation of the ligand were favoured over cation coordination, and metal complexes were not isolable.

2.5. Synthesis of L1CoCl₂

CoCl₂·6H₂O (0.187 g, 0.785 mmol, 2 equiv.) and **L1** (0.100 g, 0.393 mmol, 1 equiv.) were each dissolved in 10 ml of a 1:1 (v/v) ethanol/methanol mixture. The solution of CoCl₂·6H₂O (clear dark purple) was added dropwise to the solution of **L1**, yielding a clear dark-blue solution. The mixture was heated to approximately 60 °C and stirred for 15 min. The solution was then filtered by gravity into a small vial and left undisturbed to

crystallize. Blue X-ray-quality crystals of **L1CoCl₂** were obtained after two weeks.

3. Results and discussion

L1 crystallized in the noncentrosymmetric orthorhombic space group *Pna*2₁ with one formula unit, C₈H₇ClN₆S, in the asymmetric unit (Fig. 3). The molecule adopts a nearly planar

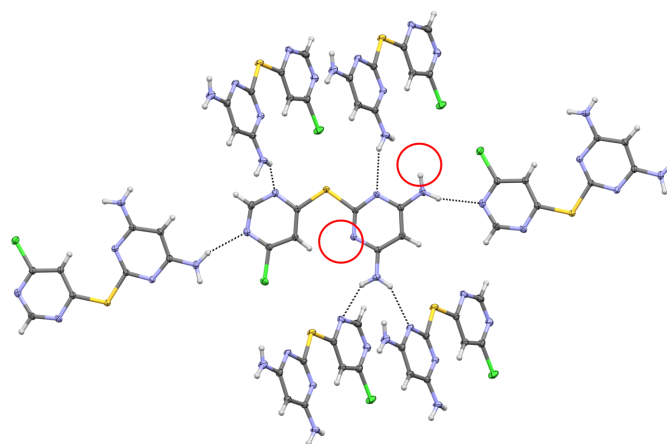


Figure 4

Extended packing diagram for **L1**, drawn with 50% probability displacement ellipsoids for the non-H atoms. Hydrogen bonds are represented as dashed lines. Unengaged hydrogen-bond donors and acceptors in the asymmetric unit are indicated by red circles.

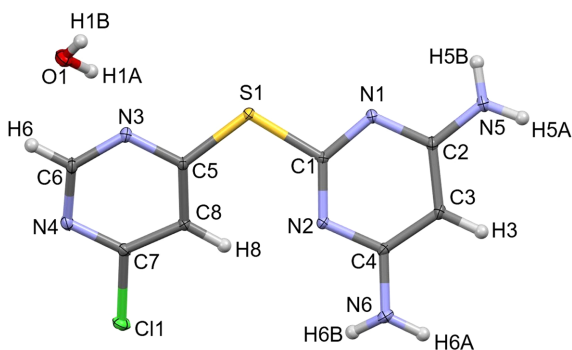


Figure 5
The asymmetric unit of **L1**·**H₂O**, drawn with 50% probability displacement ellipsoids for the non-H atoms.

orientation; considering the plane formed by the two pyrimidine rings and atom S1, the root-mean-square deviation (RMSD) is 0.046 Å. The chloro-substituted ring is oriented such that C8—H8 points toward amine-functionalized pyrimidinyl atom N2, but no intramolecular hydrogen bond is formed ($\angle \text{C8—H8} \cdots \text{N2} = 125^\circ$).

Although the number of hydrogen-bond donors and acceptors is balanced in the asymmetric unit, examination of the packing motif reveals that neither pyrimidinyl atom N2 nor the amine hydrogen-donor N5—H5A group participates in hydrogen bonding (Fig. 4). In contrast, simple intermolecular hydrogen-bond graph-set motifs *C*(6), *C*(8) and *C*(10) account for interactions involving the remaining donors and acceptors (Table 2). We, and others, have previously reported challenges related to the self-complementarity of molecules designed for anion sensing, namely, that such sensors may preferentially engage in hydrogen bonding with one another unless some acceptor sites are occupied through coordination to metal cations (Hiscock *et al.*, 2019; Mercer & Loeb, 2010; Qureshi *et al.*, 2016). Notably, the unengaged hydrogen-bond donor in **L1** suggests potential for selective

anion interactions, even in the absence of cation coordination to the available hydrogen-bond acceptors.

L1·**H₂O** crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with one formula unit, $\text{C}_8\text{H}_7\text{ClN}_6\text{S} \cdot \text{H}_2\text{O}$, in the asymmetric unit (Fig. 5). Similar to the unsolvated structure of **L1** (*vide supra*), the chloro-substituted ring is again oriented such that C8—H8 points toward amine-functionalized pyrimidinyl atom N2, but no intramolecular hydrogen bond is formed ($\angle \text{C8—H8} \cdots \text{N2} = 125^\circ$). In contrast, **L1** now adopts a twisted conformation, with a dihedral angle of $25.37(2)^\circ$ between the planes of the two pyrimidine rings.

In the structure of **L1**·**H₂O**, all amine protons are engaged in intermolecular interactions, either with pyrimidinyl N-atom acceptors from neighbouring **L1** molecules or with the O atom of the lattice water molecule. However, as in the unsolvated structure, pyrimidinyl atom N2 again does not participate in hydrogen bonding (Fig. 6). Accounting for the amine donors, the primary intermolecular hydrogen-bonding network is described by the graph-set motifs $R_2^2(8)$, *C*(10) and *D*(2) (Table 2). The continued absence of hydrogen bonding at the N2 acceptor site remains notable, especially given the presence of the lattice water molecule.

The [**L1**+**H**][**NO₃**] salt crystallized in the centrosymmetric monoclinic space group $P2_1/c$ with two formula units of $\text{C}_8\text{H}_8\text{ClN}_6\text{S} \cdot \text{NO}_3$ in the asymmetric unit (Fig. 7). One nitrate anion is ordered, while the second is disordered over two refined orientations, with occupancies of 0.672(3) and 0.328(3), respectively. Unlike **L1** and its water solvate, the amine-functionalized *endo* pyrimidinyl atom (N1 and N7) is now protonated and engaged in intramolecular hydrogen bonding with the chlorine-bearing pyrimidinyl ring in both formula units of [**L1**+**H**][**NO₃**] (both $\angle \text{N1—H1} \cdots \text{N3} = \angle \text{N7—H7} \cdots \text{N9} = 142^\circ$).

In the structure of [**L1**+**H**][**NO₃**], all strong hydrogen-bond donors and acceptors participate in intra- or intermolecular interactions (Fig. 8). Accounting for all N—H donors, the primary intermolecular hydrogen-bonding network is described by the graph-set motifs $R_2^2(8)$, *C*(10), *S*(6) and *D*(2) (Table 2). While included in Fig. 8, N—H $\cdots$ Cl interactions are

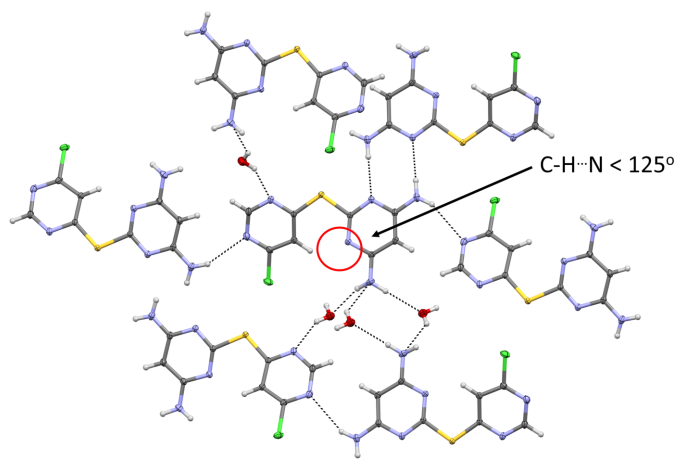


Figure 6
Extended packing diagram for **L1**·**H₂O**, drawn with 50% probability displacement ellipsoids for the non-H atoms. Hydrogen bonds are represented as dashed lines. The unengaged hydrogen-bond acceptor in the asymmetric unit is indicated by a red circle.

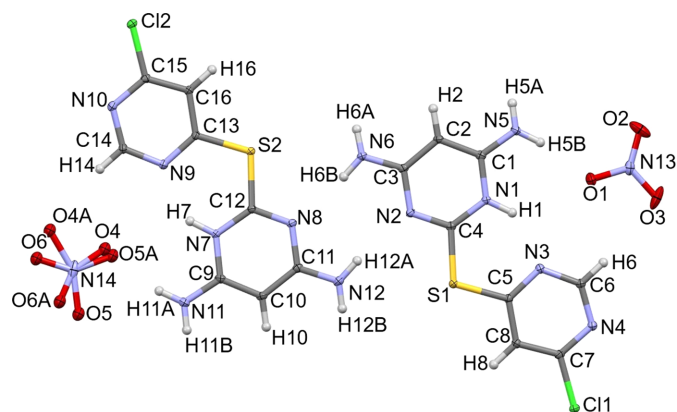


Figure 7
The asymmetric unit of [**L1**+**H**][**NO₃**], drawn with 50% probability displacement ellipsoids for the non-H atoms.

weak, with bond angles less than 135° , and are therefore omitted from Table 2.

Considering all atoms in the asymmetric unit, the molecules adopt a nearly planar orientation, with an RMSD of 0.161 Å. Packing analysis shows that the molecular planes are separated by 3.1496 (16) Å and shifted by 2.349 (2) Å. Notably, **L1** is now oriented to form a coordination pocket defined by N1–C4–S1–C5–N3 (and equivalent atoms in the second formula unit); however, protonation of N1 (and N7) renders both N1 and N3 (or N7 and N9) inaccessible for intermolecular self-complementary hydrogen bonding, and instead facilitates amine–anion hydrogen bonding.

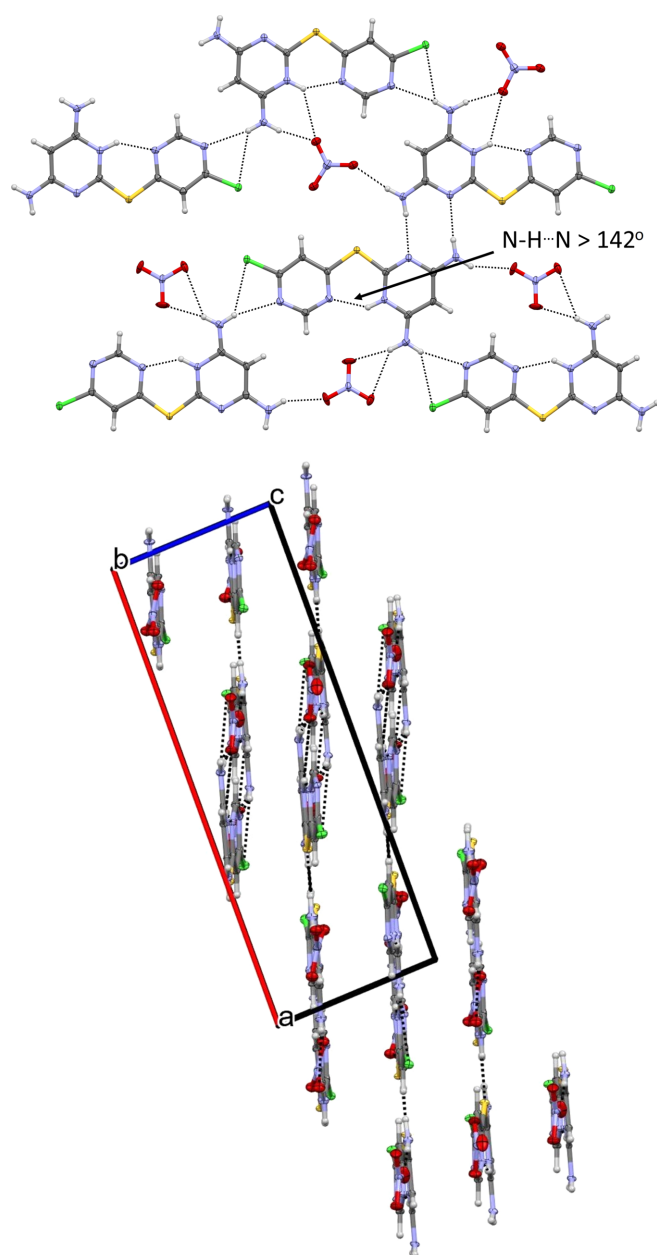


Figure 8
Extended packing diagrams for **[L1+H][NO₃]**, drawn with 50% probability displacement ellipsoids for the non-H atoms. Hydrogen bonds are represented as dashed lines. The minor disorder component has been omitted for clarity.

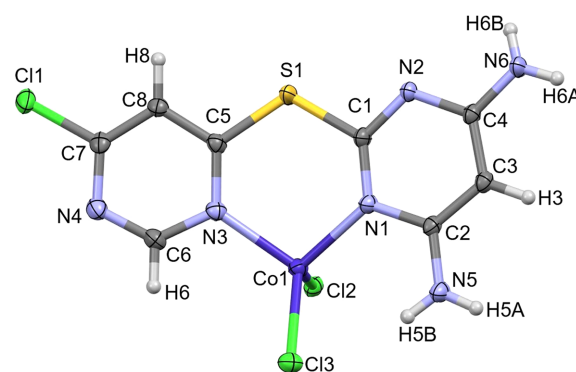


Figure 9
The asymmetric unit for **L1CoCl₂**, drawn with 50% probability displacement ellipsoids for the non-H atoms.

The complex **L1CoCl₂** also crystallized in the centrosymmetric monoclinic space group $P2_1/c$, but with one $C_8H_7ClN_5SCoCl_2$ formula unit in the asymmetric unit (Fig. 9). This complex adopts a conformation similar to that of the **[L1+H][NO₃]** salt, however, the coordination pocket defined by N1–C1–S1–C5–N3 is now bound to Co1 in a bidentate manner, forming a six-membered chelate ring.

The non-H atoms of **L1** adopt a nearly planar arrangement (RMSD = 0.104 Å), while the Co^{II} ion is puckered out of this plane, lying 0.6828 (19) Å below it. The Co1 atom adopts an approximately tetrahedral geometry, with bond angles ranging from 99.89 (13) to 115.50 (10) $^\circ$, and its charge is balanced by coordination to two chloride ions. The Co–Cl bond lengths are 2.2552 (13) and 2.2190 (13) Å, while the Co–N bond lengths are 2.013 (3) and 2.021 (3) Å.

A search of the Cambridge Structural Database (CSD, Version 5.46 with February 2025 updates; Groom *et al.*, 2016)

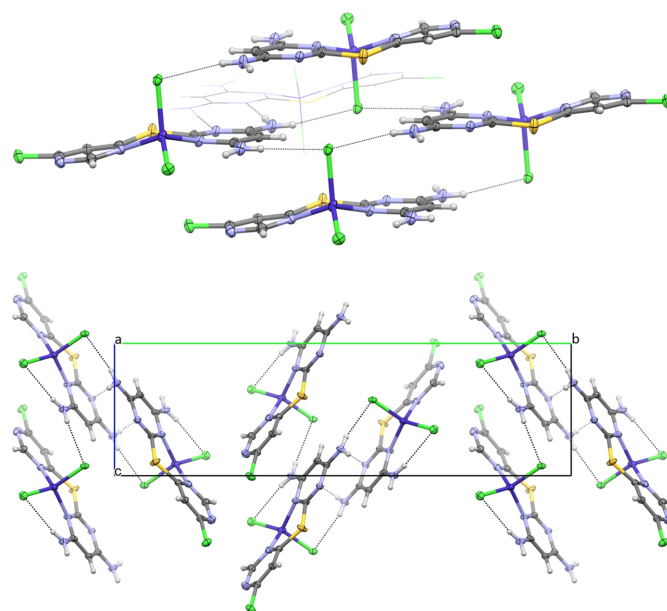


Figure 10
Extended packing diagrams for **L1CoCl₂**, drawn with 50% displacement ellipsoids, except for one molecule forming a dimer in the upper panel with wireframe representation for clarity. Hydrogen bonds are represented as dashed lines.

using *ConQuest* (Bruno *et al.*, 2002) was conducted for similar systems; specifically, four-coordinated Co complexes with two chloride ligands and two N-atom donors forming a six-membered chelate ring. This search yielded 155 Co—N and Co—Cl observations, with mean Co—Cl and Co—N bond lengths of 2.25 (4) and 2.02 (4) Å, respectively. The values observed for **L1CoCl₂** are in excellent agreement with these literature/database-reported results.

In the structure of **L1CoCl₂**, all N—H donors participate in hydrogen bonding, and the primary resulting network is described by the graph-set motifs $R_2^2(8)$, $C(10)$ and $S(6)$ (Table 2). Self-complementary rings formed *via* $N6-H6B \cdots N2^{xii}$ [symmetry code: (xii) $-x+2, -y+1, -z+2$] generate dimers, which further engage in $N5-H5A \cdots Cl2^x$ [symmetry code: (x) $x, y, z+1$] interactions with adjacent layers. This results in an $R_4^2(16)$ graph-set motif, shown in the upper panel of Fig. 10. The layers are staggered through application of the 2_1 -screw axis (Fig. 10). Notably, neither pyrimidinyl atom N4 nor adjacent atom Cl1 participates in any significant intermolecular interactions.

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was performed using *CrystalExplorer17* (Spackman *et al.*, 2021). Examination of the Hirshfeld surfaces clearly shows a 180° bond rotation about the C—S bond to the chloro-substituted pyrimidine ring in the fully hydrogen-bond-satisfied structure (*i.e.* the nitrate salt), aligning this conformation with that observed for the cobalt complex. In contrast, structures in which the ligand's hydrogen-bonding capacity is not fully utilized, and where no internal hydrogen bond is present, exhibit the opposite conformation of the chloropyrimidine ring. This difference is consistent with steric considerations: in the nitrate salt, the amine-functionalized pyrimidine ring is protonated, which would otherwise result in a steric clash with the proton on the chloro-substituted ring.

It is worth noting that in both conformations, the ligand adopts a planar geometry, which is consistent with the presence of π – π (C $\cdots$ C) interactions, as revealed by the Hirshfeld surface analysis. When curvedness is mapped, flat green regions are observed at the sites of π – π stacking [Fig. 11(c)].

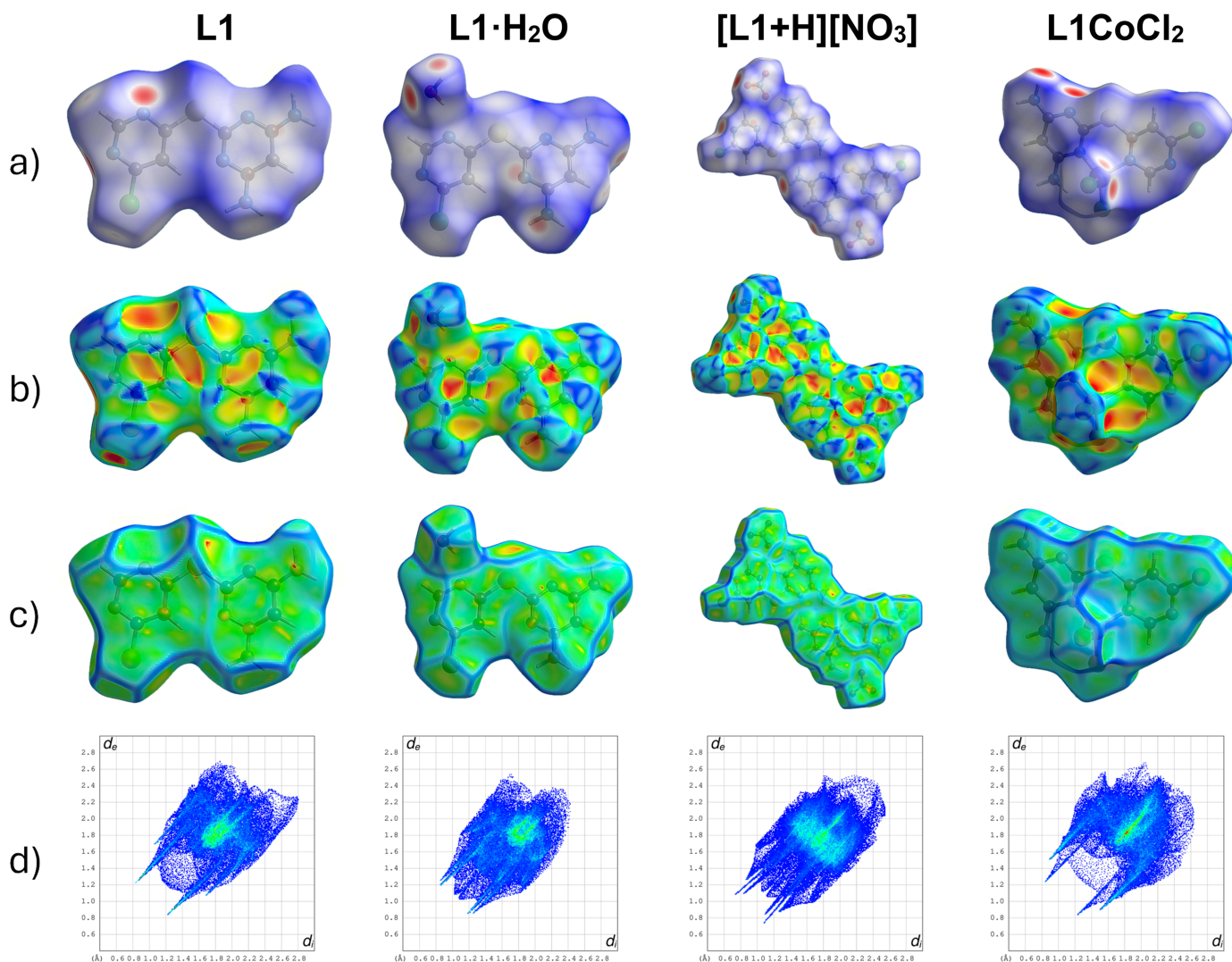


Figure 11

Hirshfeld surfaces mapped with (a) d_{norm} ranging from -0.448 (red) to 1.47 (blue), (b) shape index, mapped from 1.0 (concave, red) through 0.0 (minimal surface) to $+1.0$ (convex, blue), (c) curvedness, mapped from -4.0 (flat, green) through 0.0 (unit sphere) to $+0.4$ (singular, blue), and (d) 2D fingerprint plots with d_e and d_i ranging from 0.6 to 2.8 Å.

Similarly, when shape index is mapped, adjacent red and blue triangles appear in these regions, indicating the location of these interactions [Fig. 11(b)]. The C...C contributions to the total intermolecular contacts are greater in **L1** and **L1·H₂O** than in the nitrate salt, [**L1+H**][NO₃] (Fig. 12; also Figs. S6–S9 and Table S1 in the supporting information). While all metal-free structures exhibit planarity (Figs. S2–S5), the nitrate salt appears more planar than the water solvate, despite the lower C...C contributions. This increased planarity likely correlates with enhanced H...O interactions (Fig. 12). In Fig. 13, strong hydrogen-bond interactions are defined as H...N/N...H, H...O/O...H, Cl...H/H...Cl and H...S/S...H. Not all interaction types are relevant for every structure (*e.g.* **L1** does not contain any O atoms).

4. Conclusion

Herein, we have reported the dissymmetric thioether *N,N'*-bidentate ligand **L1**, which exhibits conformational flexibility and variable hydrogen-bonding behaviour across a series of structurally characterized compounds, including its neutral form, water solvate, protonated nitrate salt and a cobalt(II) complex. In the uncoordinated and unprotonated forms, the hydrogen-bond capacity of **L1** is unfulfilled. Upon protonation or metal coordination, however, the ligand adopts a conformation that enables full participation of its hydrogen-bond donors, demonstrating the structural adaptability of **L1** in response to its environment. These insights are foundational to further exploration of **L1** as a platform for molecular recognition and ion sensing.

Future work is planned for ligand elaboration *via* the **L1** chloride substituent, which provides a synthetic handle for further functionalization. These efforts are focused on expanding the utility of this ligand family in supramolecular and coordination-based applications.

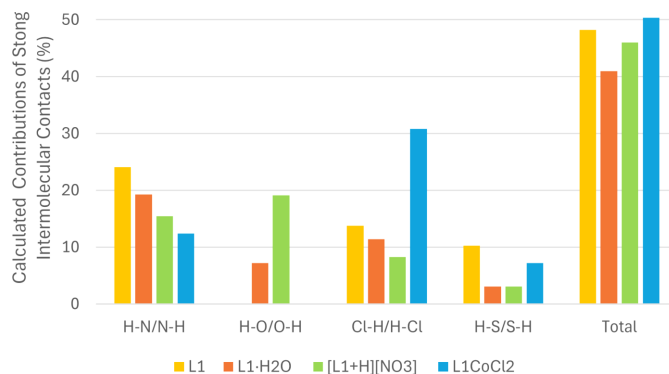


Figure 13

The calculated contributions of the strong intermolecular contacts.

Acknowledgements

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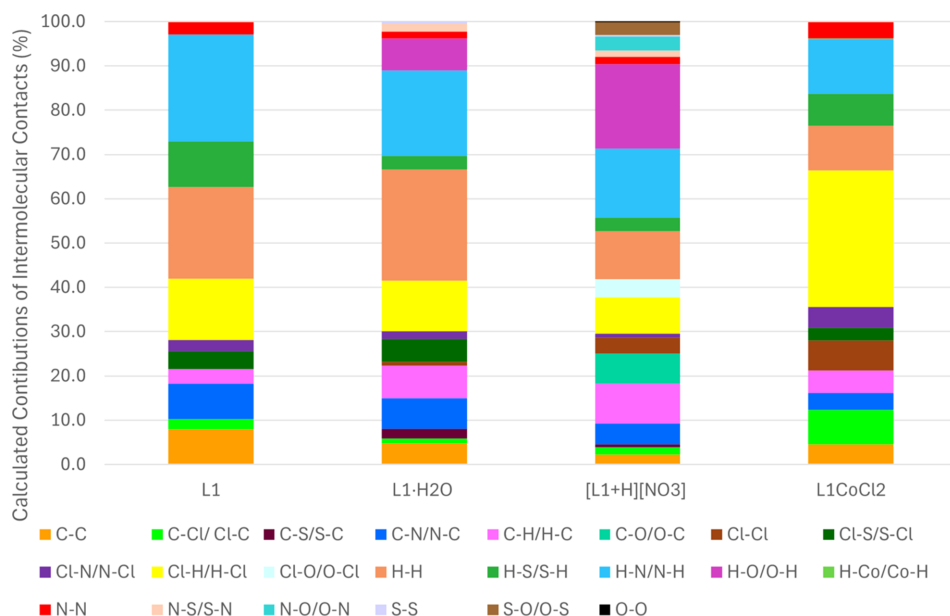


Figure 12

The calculated contributions of all the intermolecular contacts.

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supporting information

Acta Cryst. (2025). C81, 598-606 [https://doi.org/10.1107/S205322962500823X]

Structural adaptability and hydrogen bonding in a dissymmetric pyrimidine thioether ligand

Kaycee Anoliefo, Kaitlyn Brown, Lana K. Hiscock, Paul D. Boyle and Louise N. Dawe

Computing details

2-[(6-Chloropyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine (I1)

Crystal data

$C_8H_7ClN_6S$

$M_r = 254.71$

Orthorhombic, $Pna2_1$

$a = 13.5864$ (6) Å

$b = 6.8262$ (3) Å

$c = 11.6234$ (5) Å

$V = 1077.99$ (8) Å³

$Z = 4$

$F(000) = 520$

$D_x = 1.569$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9962 reflections

$\theta = 3.0\text{--}31.8^\circ$

$\mu = 0.53$ mm⁻¹

$T = 110$ K

Prism, brown

$0.19 \times 0.17 \times 0.08$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS2016; Bruker, 2016)

$T_{\min} = 0.688$, $T_{\max} = 0.747$

87768 measured reflections

5788 independent reflections

5131 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 37.8^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -23 \rightarrow 23$

$k = -11 \rightarrow 11$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.075$

$S = 1.04$

5788 reflections

161 parameters

7 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.1181P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.41$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Absolute structure: Flack x determined using
2256 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.02 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.40939 (3)	−0.07853 (6)	0.31715 (4)	0.02268 (9)
S1	0.12251 (3)	0.41689 (5)	0.48412 (3)	0.01736 (8)
N1	0.17526 (9)	0.72089 (18)	0.59177 (11)	0.0151 (2)
N2	0.31136 (9)	0.52365 (19)	0.53045 (11)	0.0144 (2)
N3	0.10009 (10)	0.08596 (18)	0.38675 (12)	0.0168 (2)
N4	0.21963 (10)	−0.13337 (19)	0.30868 (13)	0.0177 (2)
N5	0.19705 (11)	1.0090 (2)	0.69007 (13)	0.0210 (3)
H5A	0.1370 (14)	1.006 (4)	0.703 (2)	0.016 (5)*
H5B	0.2322 (19)	1.095 (4)	0.721 (2)	0.029 (7)*
N6	0.47095 (10)	0.6070 (2)	0.57357 (13)	0.0194 (2)
H6A	0.5131 (17)	0.688 (4)	0.587 (2)	0.032 (7)*
H6B	0.4875 (18)	0.520 (3)	0.5244 (19)	0.021 (6)*
C1	0.21766 (11)	0.5673 (2)	0.54075 (12)	0.0133 (2)
C2	0.23859 (12)	0.8519 (2)	0.63878 (12)	0.0149 (2)
C3	0.34030 (12)	0.8237 (2)	0.63408 (13)	0.0160 (2)
H3	0.384593	0.915665	0.667005	0.019*
C4	0.37414 (10)	0.6558 (2)	0.57935 (12)	0.0141 (2)
C5	0.17314 (10)	0.2069 (2)	0.42015 (12)	0.0141 (2)
C6	0.12778 (12)	−0.0766 (2)	0.33240 (15)	0.0188 (3)
H6	0.076566	−0.161581	0.307786	0.023*
C7	0.28922 (11)	−0.0108 (2)	0.34474 (12)	0.0155 (2)
C8	0.27204 (11)	0.1646 (2)	0.40109 (13)	0.0155 (2)
H8	0.323640	0.249329	0.424871	0.019*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01660 (15)	0.02296 (18)	0.02847 (18)	0.00580 (12)	−0.00100 (14)	−0.00802 (15)
S1	0.01064 (13)	0.01534 (15)	0.02609 (17)	0.00126 (11)	−0.00245 (13)	−0.00715 (13)
N1	0.0132 (5)	0.0128 (5)	0.0192 (5)	0.0026 (4)	−0.0021 (4)	−0.0030 (4)
N2	0.0113 (5)	0.0132 (5)	0.0187 (5)	0.0003 (4)	−0.0006 (4)	−0.0033 (4)
N3	0.0159 (5)	0.0137 (5)	0.0207 (6)	−0.0029 (4)	0.0011 (4)	−0.0021 (4)
N4	0.0190 (5)	0.0132 (4)	0.0210 (6)	−0.0006 (4)	0.0006 (5)	−0.0032 (4)
N5	0.0191 (6)	0.0153 (6)	0.0286 (7)	0.0032 (5)	−0.0015 (5)	−0.0091 (5)
N6	0.0106 (5)	0.0199 (6)	0.0277 (6)	−0.0017 (4)	0.0008 (5)	−0.0044 (5)
C1	0.0117 (5)	0.0117 (5)	0.0165 (5)	0.0007 (4)	−0.0014 (4)	−0.0019 (4)
C2	0.0160 (6)	0.0128 (5)	0.0160 (6)	0.0014 (5)	−0.0010 (4)	−0.0018 (4)
C3	0.0150 (6)	0.0140 (5)	0.0191 (6)	−0.0011 (5)	−0.0021 (5)	−0.0027 (5)
C4	0.0111 (5)	0.0145 (6)	0.0166 (5)	−0.0008 (4)	0.0001 (4)	−0.0002 (4)

C5	0.0148 (5)	0.0118 (5)	0.0158 (5)	0.0001 (4)	−0.0002 (5)	−0.0008 (4)
C6	0.0175 (6)	0.0147 (6)	0.0242 (7)	−0.0037 (5)	0.0016 (5)	−0.0031 (5)
C7	0.0157 (6)	0.0140 (5)	0.0168 (6)	0.0015 (5)	−0.0008 (4)	−0.0019 (4)
C8	0.0137 (5)	0.0142 (5)	0.0185 (6)	0.0009 (4)	−0.0010 (5)	−0.0035 (4)

Geometric parameters (Å, °)

Cl1—C7	1.7270 (15)	N5—H5B	0.84 (2)
S1—C1	1.7773 (15)	N5—C2	1.350 (2)
S1—C5	1.7551 (14)	N6—H6A	0.81 (2)
N1—C1	1.3351 (18)	N6—H6B	0.853 (19)
N1—C2	1.3563 (19)	N6—C4	1.359 (2)
N2—C1	1.3130 (19)	C2—C3	1.396 (2)
N2—C4	1.3657 (19)	C3—H3	0.9500
N3—C5	1.3482 (19)	C3—C4	1.389 (2)
N3—C6	1.331 (2)	C5—C8	1.392 (2)
N4—C6	1.335 (2)	C6—H6	0.9500
N4—C7	1.331 (2)	C7—C8	1.384 (2)
N5—H5A	0.830 (18)	C8—H8	0.9500
C5—S1—C1	110.10 (7)	C4—C3—C2	117.35 (13)
C1—N1—C2	115.03 (13)	C4—C3—H3	121.3
C1—N2—C4	114.68 (12)	N2—C4—C3	121.95 (13)
C6—N3—C5	116.05 (14)	N6—C4—N2	114.96 (13)
C7—N4—C6	114.61 (13)	N6—C4—C3	123.06 (14)
H5A—N5—H5B	120 (3)	N3—C5—S1	109.49 (11)
C2—N5—H5A	117.9 (18)	N3—C5—C8	122.52 (13)
C2—N5—H5B	121 (2)	C8—C5—S1	127.97 (11)
H6A—N6—H6B	115 (3)	N3—C6—N4	127.15 (14)
C4—N6—H6A	120.3 (19)	N3—C6—H6	116.4
C4—N6—H6B	117.3 (17)	N4—C6—H6	116.4
N1—C1—S1	107.72 (11)	N4—C7—Cl1	116.41 (11)
N2—C1—S1	122.70 (11)	N4—C7—C8	124.97 (14)
N2—C1—N1	129.58 (14)	C8—C7—Cl1	118.62 (11)
N1—C2—C3	121.41 (13)	C5—C8—H8	122.7
N5—C2—N1	115.88 (14)	C7—C8—C5	114.68 (13)
N5—C2—C3	122.72 (14)	C7—C8—H8	122.7
C2—C3—H3	121.3		
Cl1—C7—C8—C5	−179.72 (11)	C2—N1—C1—N2	0.8 (2)
S1—C5—C8—C7	−177.78 (12)	C2—C3—C4—N2	0.8 (2)
N1—C2—C3—C4	0.0 (2)	C2—C3—C4—N6	−176.92 (14)
N3—C5—C8—C7	0.3 (2)	C4—N2—C1—S1	−179.91 (11)
N4—C7—C8—C5	0.7 (2)	C4—N2—C1—N1	−0.1 (2)
N5—C2—C3—C4	179.73 (15)	C5—S1—C1—N1	−177.86 (10)
C1—S1—C5—N3	174.57 (10)	C5—S1—C1—N2	2.01 (15)
C1—S1—C5—C8	−7.15 (16)	C5—N3—C6—N4	0.8 (3)
C1—N1—C2—N5	179.54 (14)	C6—N3—C5—S1	177.41 (12)

C1—N1—C2—C3	−0.7 (2)	C6—N3—C5—C8	−1.0 (2)
C1—N2—C4—N6	177.14 (14)	C6—N4—C7—C11	179.50 (12)
C1—N2—C4—C3	−0.8 (2)	C6—N4—C7—C8	−0.9 (2)
C2—N1—C1—S1	−179.36 (11)	C7—N4—C6—N3	0.1 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N5—H5B $\cdots$ N4 ⁱ	0.84 (2)	2.21 (2)	3.023 (2)	162 (3)
N6—H6A $\cdots$ N1 ⁱⁱ	0.81 (2)	2.29 (2)	3.0215 (19)	150 (2)
N6—H6B $\cdots$ N3 ⁱⁱⁱ	0.85 (2)	2.33 (2)	3.087 (2)	148 (2)

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

2-[(6-Chloropyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine monohydrate (I1-h2o)*Crystal data*

C₈H₇ClN₆S·H₂O

M_r = 272.72

Monoclinic, *P*2₁/*n*

a = 3.8868 (15) Å

b = 14.652 (6) Å

c = 19.154 (7) Å

β = 90.147 (7)°

V = 1090.8 (8) Å³

Z = 4

F(000) = 560

D_x = 1.661 Mg m^{−3}

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9942 reflections

θ = 2.5–40.5°

μ = 0.54 mm^{−1}

T = 110 K

Prism, colourless

0.28 × 0.13 × 0.13 mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS2016; Bruker, 2016)

T_{min} = 0.685, *T_{max}* = 0.749

128142 measured reflections

8646 independent reflections

6849 reflections with *I* > 2σ(*I*)

R_{int} = 0.051

$\theta_{\max}$ = 44.2°, $\theta_{\min}$ = 3.5°

h = −7→7

k = −28→28

l = −37→37

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.030

wR(*F*²) = 0.088

S = 1.04

8646 reflections

178 parameters

7 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0456*P*)² + 0.1509*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 0.64 e Å^{−3}

Δρ_{min} = −0.36 e Å^{−3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.18664 (4)	0.06560 (2)	0.75363 (2)	0.02157 (4)
S1	0.78760 (4)	0.38676 (2)	0.67060 (2)	0.01361 (3)
N1	1.02282 (14)	0.38886 (3)	0.54752 (3)	0.01433 (8)
C1	0.93914 (14)	0.32753 (4)	0.59566 (3)	0.01210 (8)
N2	0.97521 (13)	0.23804 (3)	0.59529 (3)	0.01359 (7)
C2	1.18552 (15)	0.35461 (4)	0.49049 (3)	0.01464 (8)
C3	1.24800 (16)	0.26085 (4)	0.48440 (3)	0.01581 (9)
H3	1.367761	0.236738	0.445360	0.019*
N3	0.52294 (14)	0.34976 (4)	0.78964 (3)	0.01505 (8)
H6A	1.221 (3)	0.0868 (9)	0.4954 (6)	0.030 (3)*
H6B	1.021 (3)	0.0831 (9)	0.5594 (7)	0.029 (3)*
C4	1.12962 (15)	0.20438 (4)	0.53711 (3)	0.01433 (8)
N4	0.23791 (15)	0.21400 (4)	0.82745 (3)	0.01776 (9)
C5	0.59432 (14)	0.30956 (4)	0.72780 (3)	0.01215 (8)
N5	1.27933 (18)	0.41456 (4)	0.44119 (3)	0.02137 (10)
H5A	1.396 (4)	0.3976 (9)	0.4057 (7)	0.033 (3)*
H5B	1.226 (4)	0.4703 (8)	0.4457 (7)	0.034 (3)*
N6	1.17208 (18)	0.11162 (4)	0.53561 (3)	0.02153 (10)
C6	0.34900 (17)	0.29988 (5)	0.83547 (3)	0.01744 (10)
H6	0.297687	0.328320	0.878783	0.021*
C7	0.32214 (15)	0.17646 (4)	0.76687 (3)	0.01485 (9)
C8	0.50268 (15)	0.21955 (4)	0.71415 (3)	0.01346 (8)
H8	0.559927	0.189789	0.671671	0.016*
O1	0.80682 (18)	0.47606 (4)	0.89314 (3)	0.02649 (11)
H1A	0.770 (4)	0.4541 (11)	0.8570 (8)	0.043 (4)*
H1B	0.964 (5)	0.5066 (13)	0.8891 (10)	0.070 (6)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02149 (7)	0.01378 (6)	0.02947 (8)	−0.00225 (4)	0.00490 (6)	0.00457 (5)
S1	0.01926 (6)	0.01003 (5)	0.01156 (5)	−0.00022 (4)	0.00443 (4)	−0.00076 (4)
N1	0.01851 (19)	0.01327 (17)	0.01123 (17)	0.00028 (14)	0.00349 (14)	0.00104 (13)
C1	0.01434 (18)	0.01203 (18)	0.00992 (17)	0.00077 (14)	0.00151 (14)	−0.00008 (14)
N2	0.01743 (19)	0.01183 (16)	0.01151 (17)	0.00173 (14)	0.00242 (14)	−0.00052 (13)
C2	0.0163 (2)	0.0168 (2)	0.01085 (19)	−0.00032 (16)	0.00253 (15)	0.00056 (16)
C3	0.0177 (2)	0.0173 (2)	0.0125 (2)	0.00197 (17)	0.00402 (16)	−0.00155 (17)
N3	0.01817 (19)	0.01606 (19)	0.01091 (17)	0.00105 (15)	0.00271 (14)	−0.00076 (14)
C4	0.0163 (2)	0.01354 (19)	0.0131 (2)	0.00232 (15)	0.00158 (16)	−0.00177 (16)
N4	0.0184 (2)	0.0203 (2)	0.0146 (2)	0.00117 (16)	0.00413 (16)	0.00408 (16)
C5	0.01372 (18)	0.01249 (18)	0.01024 (18)	0.00119 (14)	0.00165 (14)	0.00061 (14)
N5	0.0294 (3)	0.0199 (2)	0.0149 (2)	0.0001 (2)	0.00846 (19)	0.00356 (18)
N6	0.0299 (3)	0.0139 (2)	0.0208 (2)	0.00392 (18)	0.0064 (2)	−0.00328 (17)
C6	0.0198 (2)	0.0210 (2)	0.0116 (2)	0.00176 (19)	0.00387 (17)	0.00088 (17)
C7	0.01426 (19)	0.0139 (2)	0.0164 (2)	0.00087 (15)	0.00170 (16)	0.00367 (16)

C8	0.0154 (2)	0.01242 (18)	0.01252 (19)	0.00019 (15)	0.00176 (15)	0.00091 (15)
O1	0.0360 (3)	0.0209 (2)	0.0226 (2)	−0.0069 (2)	0.0035 (2)	0.00107 (19)

Geometric parameters (Å, °)

Cl1—C7	1.7261 (9)	C4—N6	1.3694 (10)
S1—C1	1.7790 (7)	N4—C6	1.3390 (11)
S1—C5	1.7459 (7)	N4—C7	1.3260 (9)
N1—C1	1.3285 (8)	C5—C8	1.3908 (10)
N1—C2	1.3596 (8)	N5—H5A	0.855 (11)
C1—N2	1.3187 (9)	N5—H5B	0.848 (11)
N2—C4	1.3596 (8)	N6—H6A	0.873 (11)
C2—C3	1.3999 (11)	N6—H6B	0.854 (11)
C2—N5	1.3410 (9)	C6—H6	0.9500
C3—H3	0.9500	C7—C8	1.3836 (9)
C3—C4	1.3849 (9)	C8—H8	0.9500
N3—C5	1.3523 (8)	O1—H1A	0.777 (14)
N3—C6	1.3285 (9)	O1—H1B	0.760 (16)
C5—S1—C1	109.52 (4)	N3—C5—C8	121.65 (5)
C1—N1—C2	115.04 (6)	C8—C5—S1	127.36 (5)
N1—C1—S1	108.19 (5)	C2—N5—H5A	121.0 (9)
N2—C1—S1	121.66 (4)	C2—N5—H5B	119.5 (10)
N2—C1—N1	129.98 (5)	H5A—N5—H5B	119.4 (13)
C1—N2—C4	114.35 (5)	H6A—N6—H6B	114.7 (13)
N1—C2—C3	120.68 (5)	C4—N6—H6A	117.3 (9)
N5—C2—N1	116.87 (6)	C4—N6—H6B	113.1 (9)
N5—C2—C3	122.45 (6)	N3—C6—N4	127.27 (6)
C2—C3—H3	121.1	N3—C6—H6	116.4
C4—C3—C2	117.87 (6)	N4—C6—H6	116.4
C4—C3—H3	121.1	N4—C7—Cl1	116.30 (5)
C6—N3—C5	116.43 (6)	N4—C7—C8	125.18 (6)
N2—C4—C3	121.93 (6)	C8—C7—Cl1	118.52 (5)
N2—C4—N6	115.51 (6)	C5—C8—H8	122.4
N6—C4—C3	122.50 (6)	C7—C8—C5	115.19 (5)
C7—N4—C6	114.21 (5)	C7—C8—H8	122.4
N3—C5—S1	110.92 (5)	H1A—O1—H1B	107.4 (18)
Cl1—C7—C8—C5	178.19 (4)	C2—C3—C4—N2	−3.83 (9)
S1—C1—N2—C4	−172.95 (4)	C2—C3—C4—N6	178.86 (6)
S1—C5—C8—C7	−173.89 (4)	N3—C5—C8—C7	2.70 (8)
N1—C1—N2—C4	1.77 (9)	N4—C7—C8—C5	−0.73 (9)
N1—C2—C3—C4	1.94 (9)	C5—S1—C1—N1	168.02 (4)
C1—S1—C5—N3	170.79 (4)	C5—S1—C1—N2	−16.24 (6)
C1—S1—C5—C8	−12.32 (6)	C5—N3—C6—N4	0.39 (10)
C1—N1—C2—C3	1.38 (9)	N5—C2—C3—C4	−177.71 (6)
C1—N1—C2—N5	−178.95 (6)	C6—N3—C5—S1	174.53 (5)
C1—N2—C4—C3	2.13 (9)	C6—N3—C5—C8	−2.57 (9)

C1—N2—C4—N6	179.62 (6)	C6—N4—C7—C11	179.85 (5)
C2—N1—C1—S1	171.75 (4)	C6—N4—C7—C8	−1.21 (9)
C2—N1—C1—N2	−3.52 (9)	C7—N4—C6—N3	1.45 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N6—H6 <i>A</i> $\cdots$ O1 ⁱ	0.87 (1)	2.19 (1)	3.0625 (13)	176 (1)
N6—H6 <i>B</i> $\cdots$ O1 ⁱⁱ	0.85 (1)	2.22 (1)	3.0472 (12)	164 (1)
N5—H5 <i>A</i> $\cdots$ N4 ⁱⁱⁱ	0.86 (1)	2.59 (1)	3.3899 (12)	157 (1)
N5—H5 <i>B</i> $\cdots$ N1 ^{iv}	0.85 (1)	2.28 (1)	3.1182 (14)	169 (1)
O1—H1 <i>A</i> $\cdots$ N3	0.78 (1)	2.22 (2)	2.9259 (11)	152 (2)

Symmetry codes: (i) $x+1/2, -y+1/2, z-1/2$; (ii) $-x+3/2, y-1/2, -z+3/2$; (iii) $x+3/2, -y+1/2, z-1/2$; (iv) $-x+2, -y+1, -z+1$.

4,6-Diamino-2-[(6-chloropyrimidin-4-yl)sulfanyl]pyrimidin-1-ium nitrate (I1h-no3)*Crystal data*

$\text{C}_8\text{H}_8\text{ClN}_6\text{S}^+\cdot\text{NO}_3^-$

$M_r = 317.72$

Monoclinic, $P2_1/c$

$a = 19.541$ (8) Å

$b = 18.048$ (9) Å

$c = 6.851$ (4) Å

$\beta = 92.765$ (11)°

$V = 2413$ (2) Å³

$Z = 8$

$F(000) = 1296$

$D_x = 1.749$ Mg m^{−3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7323 reflections

$\theta = 3.3\text{--}26.9^\circ$

$\mu = 0.51$ mm^{−1}

$T = 110$ K

Needle, colourless

$0.25 \times 0.07 \times 0.06$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS2016; Bruker, 2016)

$T_{\min} = 0.674$, $T_{\max} = 0.746$

90727 measured reflections

6784 independent reflections

4861 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.090$

$\theta_{\max} = 29.6^\circ$, $\theta_{\min} = 1.0^\circ$

$h = -27 \rightarrow 27$

$k = -25 \rightarrow 25$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.105$

$S = 1.03$

6784 reflections

399 parameters

44 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 3.2579P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.88$ e Å^{−3}

$\Delta\rho_{\min} = -0.92$ e Å^{−3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.67068 (3)	−0.19663 (3)	0.62394 (9)	0.02048 (12)	
N1	0.57324 (9)	0.17417 (10)	0.6113 (3)	0.0142 (4)	
H1	0.5549 (14)	0.1303 (14)	0.632 (4)	0.029 (8)*	
C1	0.53817 (11)	0.23982 (12)	0.6347 (3)	0.0146 (4)	
S1	0.68783 (3)	0.09654 (3)	0.51455 (8)	0.01666 (12)	
N2	0.67313 (9)	0.23610 (10)	0.5251 (3)	0.0147 (4)	
C2	0.57237 (11)	0.30550 (12)	0.6008 (3)	0.0152 (4)	
H2	0.549814	0.351767	0.613270	0.018*	
N3	0.57738 (9)	0.02630 (10)	0.6478 (3)	0.0159 (4)	
C3	0.64029 (11)	0.30273 (12)	0.5482 (3)	0.0144 (4)	
N4	0.57333 (9)	−0.10433 (10)	0.6978 (3)	0.0158 (4)	
C4	0.63858 (11)	0.17595 (12)	0.5571 (3)	0.0142 (4)	
C5	0.64095 (11)	0.01901 (12)	0.5860 (3)	0.0140 (4)	
N5	0.47394 (10)	0.23638 (11)	0.6857 (3)	0.0183 (4)	
H5A	0.4539 (12)	0.2764 (10)	0.707 (4)	0.019 (7)*	
H5B	0.4581 (13)	0.1951 (10)	0.715 (4)	0.024 (7)*	
C6	0.54686 (12)	−0.03618 (12)	0.7033 (3)	0.0169 (4)	
H6	0.502211	−0.031591	0.750978	0.020*	
N6	0.67737 (10)	0.36225 (11)	0.5139 (3)	0.0182 (4)	
H6A	0.6600 (14)	0.4040 (11)	0.537 (4)	0.029 (8)*	
H6B	0.7184 (9)	0.3543 (15)	0.487 (4)	0.028 (8)*	
C7	0.63639 (11)	−0.10881 (12)	0.6326 (3)	0.0159 (4)	
C8	0.67413 (11)	−0.04891 (12)	0.5745 (3)	0.0159 (4)	
H8	0.719234	−0.053635	0.530184	0.019*	
Cl2	0.82160 (3)	0.77969 (3)	0.35593 (8)	0.01783 (12)	
S2	0.80664 (3)	0.48512 (3)	0.43453 (8)	0.01653 (12)	
N7	0.92291 (9)	0.41096 (10)	0.3371 (3)	0.0150 (4)	
H7	0.9406 (15)	0.4553 (14)	0.317 (4)	0.034 (8)*	
N8	0.82302 (10)	0.34605 (10)	0.4094 (3)	0.0157 (4)	
N9	0.91796 (9)	0.55890 (10)	0.3174 (3)	0.0159 (4)	
C9	0.95803 (12)	0.34651 (12)	0.3037 (3)	0.0168 (4)	
C10	0.92530 (12)	0.27990 (12)	0.3327 (3)	0.0180 (4)	
H10	0.949064	0.234384	0.319547	0.022*	
N10	0.92107 (10)	0.69010 (10)	0.2829 (3)	0.0173 (4)	
N11	1.02180 (11)	0.35273 (12)	0.2470 (3)	0.0224 (4)	
H11A	1.0403 (15)	0.3941 (11)	0.232 (4)	0.035 (9)*	
H11B	1.0433 (15)	0.3131 (12)	0.226 (5)	0.040 (9)*	
C11	0.85691 (11)	0.28038 (12)	0.3815 (3)	0.0163 (4)	
C12	0.85709 (11)	0.40704 (12)	0.3867 (3)	0.0142 (4)	
N12	0.81984 (11)	0.21968 (11)	0.4026 (3)	0.0217 (4)	
H12A	0.7796 (9)	0.2277 (14)	0.436 (4)	0.018 (7)*	
H12B	0.8412 (15)	0.1796 (12)	0.390 (5)	0.044 (10)*	
C13	0.85406 (11)	0.56410 (12)	0.3772 (3)	0.0141 (4)	
C14	0.94844 (12)	0.62249 (12)	0.2730 (3)	0.0177 (4)	
H14	0.993889	0.619340	0.230268	0.021*	

C15	0.85756 (11)	0.69267 (12)	0.3444 (3)	0.0153 (4)	
C16	0.82032 (11)	0.63140 (12)	0.3961 (3)	0.0154 (4)	
H16	0.775190	0.634887	0.440968	0.018*	
N14	1.11786 (13)	0.51157 (13)	0.1275 (3)	0.0335 (6)	
O4	1.0666 (2)	0.50735 (19)	0.2148 (7)	0.0309 (4)	0.672 (3)
O5	1.15145 (15)	0.44774 (17)	0.0995 (4)	0.0309 (4)	0.672 (3)
O6	1.14502 (15)	0.56565 (15)	0.0600 (4)	0.0309 (4)	0.672 (3)
O4A	1.1066 (3)	0.5894 (3)	0.1161 (9)	0.0309 (4)	0.328 (3)
O5A	1.0658 (5)	0.4903 (4)	0.2352 (14)	0.0309 (4)	0.328 (3)
O6A	1.1585 (3)	0.4838 (4)	0.0614 (9)	0.0309 (4)	0.328 (3)
O1	0.43931 (9)	0.09248 (10)	0.7915 (3)	0.0311 (4)	
O2	0.33812 (11)	0.10814 (15)	0.8928 (3)	0.0501 (6)	
O3	0.38542 (13)	−0.00087 (12)	0.8940 (3)	0.0511 (7)	
N13	0.38612 (11)	0.06777 (12)	0.8608 (3)	0.0231 (4)	

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0168 (3)	0.0119 (2)	0.0329 (3)	0.0017 (2)	0.0042 (2)	−0.0001 (2)
N1	0.0144 (9)	0.0121 (9)	0.0161 (8)	0.0011 (7)	0.0018 (7)	−0.0001 (7)
C1	0.0151 (10)	0.0174 (10)	0.0111 (9)	0.0022 (8)	−0.0005 (8)	0.0008 (8)
S1	0.0157 (3)	0.0112 (2)	0.0236 (3)	−0.0001 (2)	0.0066 (2)	−0.0002 (2)
N2	0.0162 (9)	0.0111 (8)	0.0166 (9)	0.0000 (7)	0.0005 (7)	−0.0007 (7)
C2	0.0166 (11)	0.0126 (10)	0.0163 (10)	0.0034 (8)	0.0012 (8)	−0.0003 (8)
N3	0.0142 (9)	0.0147 (9)	0.0190 (9)	0.0000 (7)	0.0032 (7)	0.0011 (7)
C3	0.0173 (11)	0.0135 (10)	0.0124 (9)	0.0003 (8)	−0.0005 (8)	−0.0012 (8)
N4	0.0145 (9)	0.0152 (9)	0.0179 (9)	−0.0008 (7)	0.0014 (7)	0.0007 (7)
C4	0.0153 (10)	0.0146 (10)	0.0127 (9)	0.0010 (8)	−0.0002 (8)	−0.0006 (7)
C5	0.0143 (10)	0.0138 (10)	0.0138 (9)	−0.0016 (8)	0.0012 (8)	−0.0005 (8)
N5	0.0162 (10)	0.0171 (10)	0.0219 (10)	0.0029 (8)	0.0054 (8)	0.0007 (8)
C6	0.0157 (11)	0.0146 (10)	0.0205 (10)	0.0004 (8)	0.0025 (8)	0.0000 (8)
N6	0.0177 (10)	0.0118 (9)	0.0255 (10)	0.0013 (8)	0.0040 (8)	−0.0013 (7)
C7	0.0170 (11)	0.0126 (10)	0.0177 (10)	0.0003 (8)	−0.0020 (8)	−0.0008 (8)
C8	0.0143 (10)	0.0152 (10)	0.0182 (10)	0.0003 (8)	0.0013 (8)	−0.0009 (8)
Cl2	0.0200 (3)	0.0109 (2)	0.0228 (3)	0.0010 (2)	0.0036 (2)	0.00074 (19)
S2	0.0133 (3)	0.0099 (2)	0.0267 (3)	−0.0001 (2)	0.0047 (2)	−0.0004 (2)
N7	0.0136 (9)	0.0111 (9)	0.0205 (9)	−0.0005 (7)	0.0027 (7)	−0.0002 (7)
N8	0.0168 (9)	0.0106 (8)	0.0197 (9)	0.0012 (7)	0.0008 (7)	−0.0009 (7)
N9	0.0139 (9)	0.0132 (9)	0.0207 (9)	−0.0006 (7)	0.0015 (7)	0.0001 (7)
C9	0.0169 (11)	0.0162 (11)	0.0175 (10)	0.0038 (8)	0.0016 (8)	−0.0018 (8)
C10	0.0196 (11)	0.0122 (10)	0.0224 (11)	0.0029 (9)	0.0017 (9)	−0.0018 (8)
N10	0.0175 (10)	0.0133 (9)	0.0211 (9)	−0.0014 (7)	0.0017 (7)	0.0016 (7)
N11	0.0158 (10)	0.0191 (11)	0.0330 (11)	0.0031 (8)	0.0070 (9)	0.0003 (9)
C11	0.0185 (11)	0.0142 (10)	0.0162 (10)	−0.0001 (8)	−0.0007 (8)	−0.0014 (8)
C12	0.0144 (10)	0.0122 (10)	0.0160 (10)	0.0014 (8)	0.0002 (8)	−0.0012 (8)
N12	0.0210 (11)	0.0122 (9)	0.0323 (11)	−0.0008 (8)	0.0048 (9)	−0.0008 (8)
C13	0.0141 (10)	0.0120 (10)	0.0161 (10)	−0.0013 (8)	−0.0004 (8)	0.0012 (8)
C14	0.0141 (11)	0.0156 (11)	0.0235 (11)	−0.0023 (8)	0.0021 (9)	0.0019 (8)

C15	0.0160 (10)	0.0141 (10)	0.0154 (10)	0.0009 (8)	−0.0012 (8)	−0.0001 (8)
C16	0.0151 (11)	0.0126 (10)	0.0185 (10)	−0.0008 (8)	0.0027 (8)	−0.0003 (8)
N14	0.0394 (14)	0.0373 (13)	0.0228 (11)	−0.0224 (11)	−0.0088 (10)	0.0090 (10)
O4	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O5	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O6	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O4A	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O5A	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O6A	0.0311 (8)	0.0226 (10)	0.0396 (9)	−0.0032 (8)	0.0070 (6)	0.0022 (7)
O1	0.0224 (9)	0.0297 (10)	0.0421 (11)	−0.0027 (8)	0.0114 (8)	0.0057 (8)
O2	0.0263 (11)	0.0871 (19)	0.0372 (12)	0.0203 (12)	0.0048 (9)	−0.0110 (12)
O3	0.0782 (18)	0.0322 (12)	0.0419 (12)	−0.0330 (12)	−0.0093 (12)	0.0133 (9)
N13	0.0250 (11)	0.0263 (11)	0.0178 (9)	−0.0093 (9)	0.0001 (8)	0.0021 (8)

Geometric parameters (Å, °)

Cl1—C7	1.723 (2)	N7—C12	1.348 (3)
N1—H1	0.88 (2)	N8—C11	1.375 (3)
N1—C1	1.382 (3)	N8—C12	1.300 (3)
N1—C4	1.347 (3)	N9—C13	1.336 (3)
C1—C2	1.386 (3)	N9—C14	1.335 (3)
C1—N5	1.320 (3)	C9—C10	1.381 (3)
S1—C4	1.758 (2)	C9—N11	1.328 (3)
S1—C5	1.755 (2)	C10—H10	0.9500
N2—C3	1.376 (3)	C10—C11	1.393 (3)
N2—C4	1.303 (3)	N10—C14	1.335 (3)
C2—H2	0.9500	N10—C15	1.331 (3)
C2—C3	1.393 (3)	N11—H11A	0.838 (16)
N3—C5	1.338 (3)	N11—H11B	0.845 (16)
N3—C6	1.339 (3)	C11—N12	1.325 (3)
C3—N6	1.323 (3)	N12—H12A	0.841 (15)
N4—C6	1.336 (3)	N12—H12B	0.842 (16)
N4—C7	1.333 (3)	C13—C16	1.391 (3)
C5—C8	1.391 (3)	C14—H14	0.9500
N5—H5A	0.837 (16)	C15—C16	1.379 (3)
N5—H5B	0.834 (16)	C16—H16	0.9500
C6—H6	0.9500	N14—O4	1.194 (5)
N6—H6A	0.844 (16)	N14—O5	1.344 (4)
N6—H6B	0.844 (16)	N14—O6	1.213 (3)
C7—C8	1.378 (3)	N14—O4A	1.423 (6)
C8—H8	0.9500	N14—O5A	1.341 (8)
Cl2—C15	1.724 (2)	N14—O6A	1.059 (6)
S2—C12	1.760 (2)	O1—N13	1.246 (3)
S2—C13	1.755 (2)	O2—N13	1.216 (3)
N7—H7	0.89 (2)	O3—N13	1.260 (3)
N7—C9	1.375 (3)		
C1—N1—H1	122.9 (18)	C14—N9—C13	116.33 (19)

C4—N1—H1	117.6 (18)	N7—C9—C10	118.3 (2)
C4—N1—C1	119.58 (19)	N11—C9—N7	117.4 (2)
N1—C1—C2	117.9 (2)	N11—C9—C10	124.3 (2)
N5—C1—N1	118.3 (2)	C9—C10—H10	120.5
N5—C1—C2	123.8 (2)	C9—C10—C11	119.0 (2)
C5—S1—C4	107.84 (11)	C11—C10—H10	120.5
C4—N2—C3	117.43 (19)	C15—N10—C14	115.47 (19)
C1—C2—H2	120.5	C9—N11—H11A	122 (2)
C1—C2—C3	119.1 (2)	C9—N11—H11B	117 (2)
C3—C2—H2	120.5	H11A—N11—H11B	121 (3)
C5—N3—C6	116.10 (19)	N8—C11—C10	120.8 (2)
N2—C3—C2	121.12 (19)	N12—C11—N8	115.3 (2)
N6—C3—N2	115.3 (2)	N12—C11—C10	123.8 (2)
N6—C3—C2	123.6 (2)	N7—C12—S2	123.70 (16)
C7—N4—C6	115.50 (19)	N8—C12—S2	111.17 (16)
N1—C4—S1	124.05 (16)	N8—C12—N7	125.1 (2)
N2—C4—N1	124.9 (2)	C11—N12—H12A	114.2 (18)
N2—C4—S1	111.05 (16)	C11—N12—H12B	115 (2)
N3—C5—S1	121.00 (16)	H12A—N12—H12B	130 (3)
N3—C5—C8	123.2 (2)	N9—C13—S2	121.52 (16)
C8—C5—S1	115.85 (17)	N9—C13—C16	123.0 (2)
C1—N5—H5A	117.7 (18)	C16—C13—S2	115.51 (16)
C1—N5—H5B	118.3 (19)	N9—C14—N10	126.1 (2)
H5A—N5—H5B	123 (3)	N9—C14—H14	116.9
N3—C6—H6	116.9	N10—C14—H14	116.9
N4—C6—N3	126.1 (2)	N10—C15—C12	115.77 (16)
N4—C6—H6	116.9	N10—C15—C16	124.4 (2)
C3—N6—H6A	118 (2)	C16—C15—C12	119.83 (17)
C3—N6—H6B	116 (2)	C13—C16—H16	122.6
H6A—N6—H6B	126 (3)	C15—C16—C13	114.7 (2)
N4—C7—C11	115.76 (16)	C15—C16—H16	122.6
N4—C7—C8	124.4 (2)	O4—N14—O5	116.4 (3)
C8—C7—C11	119.82 (18)	O4—N14—O6	129.5 (3)
C5—C8—H8	122.7	O6—N14—O5	114.2 (3)
C7—C8—C5	114.7 (2)	O5A—N14—O4A	101.2 (5)
C7—C8—H8	122.7	O6A—N14—O4A	124.1 (5)
C13—S2—C12	107.59 (11)	O6A—N14—O5A	134.7 (5)
C9—N7—H7	122.4 (19)	O1—N13—O3	115.9 (2)
C12—N7—H7	118.2 (19)	O2—N13—O1	121.3 (2)
C12—N7—C9	119.17 (19)	O2—N13—O3	122.8 (2)
C12—N8—C11	117.40 (19)		
C11—C7—C8—C5	179.37 (16)	C12—C15—C16—C13	178.75 (16)
N1—C1—C2—C3	−1.0 (3)	S2—C13—C16—C15	−178.03 (16)
C1—N1—C4—S1	−177.82 (15)	N7—C9—C10—C11	4.3 (3)
C1—N1—C4—N2	0.6 (3)	N9—C13—C16—C15	1.2 (3)
C1—C2—C3—N2	1.5 (3)	C9—N7—C12—S2	179.65 (16)
C1—C2—C3—N6	−179.6 (2)	C9—N7—C12—N8	1.2 (3)

S1—C5—C8—C7	179.61 (16)	C9—C10—C11—N8	−2.9 (3)
N3—C5—C8—C7	−0.2 (3)	C9—C10—C11—N12	176.4 (2)
C3—N2—C4—N1	−0.1 (3)	N10—C15—C16—C13	−0.7 (3)
C3—N2—C4—S1	178.48 (15)	N11—C9—C10—C11	−176.3 (2)
N4—C7—C8—C5	−0.8 (3)	C11—N8—C12—S2	−178.37 (15)
C4—N1—C1—C2	0.0 (3)	C11—N8—C12—N7	0.3 (3)
C4—N1—C1—N5	179.2 (2)	C12—S2—C13—N9	−2.7 (2)
C4—S1—C5—N3	3.8 (2)	C12—S2—C13—C16	176.57 (16)
C4—S1—C5—C8	−175.95 (16)	C12—N7—C9—C10	−3.4 (3)
C4—N2—C3—C2	−1.0 (3)	C12—N7—C9—N11	177.1 (2)
C4—N2—C3—N6	−179.9 (2)	C12—N8—C11—C10	0.6 (3)
C5—S1—C4—N1	−7.6 (2)	C12—N8—C11—N12	−178.8 (2)
C5—S1—C4—N2	173.78 (15)	C13—S2—C12—N7	6.9 (2)
C5—N3—C6—N4	−1.7 (3)	C13—S2—C12—N8	−174.39 (15)
N5—C1—C2—C3	179.8 (2)	C13—N9—C14—N10	0.0 (3)
C6—N3—C5—S1	−178.43 (16)	C14—N9—C13—S2	178.29 (16)
C6—N3—C5—C8	1.3 (3)	C14—N9—C13—C16	−0.9 (3)
C6—N4—C7—C11	−179.66 (16)	C14—N10—C15—C12	−179.54 (16)
C6—N4—C7—C8	0.5 (3)	C14—N10—C15—C16	−0.1 (3)
C7—N4—C6—N3	0.8 (3)	C15—N10—C14—N9	0.4 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ N3	0.88 (2)	1.93 (3)	2.681 (3)	142 (3)
N5—H5 <i>A</i> $\cdots$ N4 ⁱ	0.84 (2)	2.32 (2)	3.134 (3)	165 (2)
N5—H5 <i>B</i> $\cdots$ O1	0.83 (2)	1.97 (2)	2.789 (3)	169 (3)
N6—H6 <i>A</i> $\cdots$ O3 ⁱ	0.84 (2)	2.00 (2)	2.843 (3)	176 (3)
N6—H6 <i>B</i> $\cdots$ N8	0.84 (2)	2.14 (2)	2.983 (3)	174 (3)
C8—H8 $\cdots$ O6 <i>A</i> ⁱⁱ	0.95	2.59	3.495 (7)	159
N7—H7 $\cdots$ N9	0.89 (2)	1.92 (3)	2.675 (3)	142 (3)
N11—H11 <i>A</i> $\cdots$ O4	0.84 (2)	2.11 (2)	2.936 (4)	167 (3)
N11—H11 <i>A</i> $\cdots$ O5 <i>A</i>	0.84 (2)	1.81 (2)	2.630 (8)	167 (3)
N11—H11 <i>B</i> $\cdots$ N10 ⁱⁱ	0.85 (2)	2.33 (2)	3.150 (3)	164 (3)
N12—H12 <i>A</i> $\cdots$ N2	0.84 (2)	2.20 (2)	3.040 (3)	174 (2)
N12—H12 <i>B</i> $\cdots$ O6 ⁱⁱ	0.84 (2)	2.10 (2)	2.872 (4)	152 (3)
N12—H12 <i>B</i> $\cdots$ O4 <i>A</i> ⁱⁱ	0.84 (2)	1.92 (2)	2.763 (6)	175 (3)
C14—H14 $\cdots$ O4 <i>A</i>	0.95	2.43	3.374 (7)	171

Symmetry codes: (i) $-x+1, y+1/2, -z+3/2$; (ii) $-x+2, y-1/2, -z+1/2$.Dichlorido[2-[(6-chloropyrimidin-4-yl- κ N³)sulfanyl]pyrimidine-4,6-diamine- κ N³]cobalt(II) (I1cocl2)

Crystal data

[CoCl₂(C₈H₇ClN₆S)]*M_r* = 384.54Monoclinic, *P*2₁/*c**a* = 7.763 (2) Å*b* = 24.510 (9) Å*c* = 7.152 (3) Å β = 97.464 (4)°*V* = 1349.4 (9) Å³*Z* = 4*F*(000) = 764

$D_x = 1.893 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 9836 reflections
 $\theta = 2.8\text{--}26.0^\circ$

$\mu = 2.01 \text{ mm}^{-1}$
 $T = 110 \text{ K}$
 Plate, blue
 $0.39 \times 0.16 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 φ and ω scans
 Absorption correction: empirical (using
 intensity measurements)
 (TWINABS2012; Bruker, 2012)
 $T_{\min} = 0.532$, $T_{\max} = 0.745$
 71073 measured reflections

2659 independent reflections
 2324 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 1.7^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 30$
 $l = 0 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.087$
 $S = 1.15$
 2659 reflections
 184 parameters
 6 restraints
 Primary atom site location: dual

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 4.4992P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.69 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.41665 (7)	0.63366 (2)	0.58786 (7)	0.02889 (15)
Cl1	0.93016 (14)	0.70190 (5)	−0.00570 (15)	0.0414 (3)
Cl2	0.27113 (12)	0.56518 (4)	0.42652 (13)	0.0301 (2)
Cl3	0.23837 (13)	0.69986 (5)	0.65200 (15)	0.0367 (3)
S1	0.84266 (15)	0.58885 (5)	0.60342 (15)	0.0407 (3)
N1	0.5682 (4)	0.60231 (14)	0.8118 (4)	0.0271 (7)
N2	0.8217 (4)	0.55009 (13)	0.9202 (4)	0.0269 (7)
N3	0.6013 (4)	0.66161 (14)	0.4373 (4)	0.0282 (7)
N4	0.6541 (5)	0.71293 (15)	0.1656 (5)	0.0359 (8)
N5	0.3451 (5)	0.61082 (17)	0.9974 (5)	0.0349 (9)
H5A	0.297 (6)	0.604 (2)	1.088 (5)	0.052*
H5B	0.302 (6)	0.6345 (17)	0.926 (6)	0.052*
N6	0.8494 (5)	0.50407 (16)	1.1995 (5)	0.0338 (8)
H6A	0.810 (6)	0.493 (2)	1.292 (5)	0.051*
H6B	0.931 (5)	0.4882 (19)	1.164 (7)	0.051*
C1	0.7255 (5)	0.58132 (16)	0.7988 (5)	0.0271 (8)
C2	0.5010 (5)	0.58947 (17)	0.9774 (5)	0.0263 (8)

C3	0.5896 (5)	0.55597 (17)	1.1102 (5)	0.0286 (9)
H3	0.541552	0.546510	1.221384	0.034*
C4	0.7511 (5)	0.53612 (16)	1.0789 (5)	0.0268 (8)
C5	0.7617 (5)	0.63997 (17)	0.4465 (5)	0.0278 (9)
C6	0.5601 (6)	0.69926 (17)	0.2999 (6)	0.0329 (9)
H6	0.452605	0.717751	0.300078	0.040*
C7	0.8083 (5)	0.68860 (17)	0.1760 (6)	0.0310 (9)
C8	0.8728 (5)	0.65369 (17)	0.3173 (5)	0.0295 (9)
H8	0.987590	0.639621	0.326348	0.035*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0252 (3)	0.0390 (3)	0.0221 (3)	0.0045 (2)	0.0015 (2)	0.0003 (2)
Cl1	0.0376 (6)	0.0487 (7)	0.0384 (6)	−0.0074 (5)	0.0070 (5)	0.0131 (5)
Cl2	0.0275 (5)	0.0398 (6)	0.0236 (5)	−0.0016 (4)	0.0064 (4)	0.0007 (4)
Cl3	0.0302 (5)	0.0395 (6)	0.0402 (6)	0.0060 (5)	0.0034 (4)	−0.0025 (5)
S1	0.0420 (6)	0.0546 (7)	0.0287 (5)	0.0219 (6)	0.0160 (5)	0.0162 (5)
N1	0.0256 (17)	0.036 (2)	0.0199 (16)	0.0042 (15)	0.0037 (13)	−0.0013 (14)
N2	0.0291 (18)	0.0313 (18)	0.0208 (16)	0.0032 (15)	0.0052 (13)	0.0022 (13)
N3	0.0269 (17)	0.0306 (18)	0.0262 (17)	−0.0001 (15)	0.0002 (13)	−0.0018 (14)
N4	0.033 (2)	0.038 (2)	0.035 (2)	−0.0021 (17)	0.0004 (15)	0.0068 (16)
N5	0.029 (2)	0.052 (2)	0.0247 (19)	0.0044 (17)	0.0055 (15)	0.0037 (17)
N6	0.037 (2)	0.043 (2)	0.0230 (18)	0.0116 (17)	0.0092 (15)	0.0077 (16)
C1	0.030 (2)	0.033 (2)	0.0186 (18)	0.0015 (18)	0.0046 (15)	−0.0001 (16)
C2	0.0243 (19)	0.035 (2)	0.0195 (18)	−0.0036 (17)	0.0024 (15)	−0.0038 (16)
C3	0.030 (2)	0.034 (2)	0.0213 (19)	−0.0033 (18)	0.0037 (16)	−0.0019 (16)
C4	0.029 (2)	0.030 (2)	0.0215 (19)	−0.0017 (17)	0.0047 (15)	−0.0010 (16)
C5	0.030 (2)	0.031 (2)	0.0210 (19)	0.0032 (18)	−0.0003 (15)	−0.0007 (16)
C6	0.034 (2)	0.032 (2)	0.032 (2)	0.0046 (19)	−0.0014 (17)	0.0022 (18)
C7	0.027 (2)	0.036 (2)	0.029 (2)	−0.0088 (18)	−0.0010 (16)	0.0011 (17)
C8	0.026 (2)	0.033 (2)	0.030 (2)	−0.0005 (17)	0.0014 (16)	0.0006 (17)

Geometric parameters ($\text{\AA}$, $^\circ$)

Co1—Cl2	2.2552 (13)	N4—C7	1.331 (5)
Co1—Cl3	2.2190 (13)	N5—H5A	0.81 (3)
Co1—N1	2.013 (3)	N5—H5B	0.81 (3)
Co1—N3	2.021 (3)	N5—C2	1.343 (5)
Cl1—C7	1.735 (4)	N6—H6A	0.81 (3)
S1—C1	1.774 (4)	N6—H6B	0.81 (3)
S1—C5	1.744 (4)	N6—C4	1.331 (5)
N1—C1	1.339 (5)	C2—C3	1.371 (5)
N1—C2	1.391 (5)	C3—H3	0.9500
N2—C1	1.315 (5)	C3—C4	1.390 (6)
N2—C4	1.367 (5)	C5—C8	1.385 (5)
N3—C5	1.347 (5)	C6—H6	0.9500
N3—C6	1.356 (5)	C7—C8	1.368 (6)

N4—C6	1.323 (5)	C8—H8	0.9500
Cl3—Co1—Cl2	111.44 (5)	N2—C1—N1	128.5 (4)
N1—Co1—Cl2	108.98 (10)	N5—C2—N1	116.4 (3)
N1—Co1—Cl3	115.50 (10)	N5—C2—C3	122.5 (4)
N1—Co1—N3	99.89 (13)	C3—C2—N1	121.0 (4)
N3—Co1—Cl2	108.81 (10)	C2—C3—H3	120.7
N3—Co1—Cl3	111.52 (10)	C2—C3—C4	118.7 (4)
C5—S1—C1	113.76 (19)	C4—C3—H3	120.7
C1—N1—Co1	122.4 (2)	N2—C4—C3	120.9 (4)
C1—N1—C2	114.7 (3)	N6—C4—N2	115.3 (3)
C2—N1—Co1	121.3 (3)	N6—C4—C3	123.8 (4)
C1—N2—C4	116.1 (3)	N3—C5—S1	124.6 (3)
C5—N3—Co1	123.7 (3)	N3—C5—C8	121.6 (4)
C5—N3—C6	115.6 (3)	C8—C5—S1	113.6 (3)
C6—N3—Co1	120.0 (3)	N3—C6—H6	116.6
C6—N4—C7	115.0 (4)	N4—C6—N3	126.8 (4)
H5A—N5—H5B	118 (5)	N4—C6—H6	116.6
C2—N5—H5A	121 (4)	N4—C7—Cl1	116.6 (3)
C2—N5—H5B	121 (4)	N4—C7—C8	124.2 (4)
H6A—N6—H6B	119 (5)	C8—C7—Cl1	119.2 (3)
C4—N6—H6A	118 (4)	C5—C8—H8	121.8
C4—N6—H6B	119 (4)	C7—C8—C5	116.4 (4)
N1—C1—S1	125.5 (3)	C7—C8—H8	121.8
N2—C1—S1	106.0 (3)		
Co1—N1—C1—S1	12.7 (5)	C1—N2—C4—N6	179.4 (4)
Co1—N1—C1—N2	−164.7 (3)	C1—N2—C4—C3	−2.3 (6)
Co1—N1—C2—N5	−15.7 (5)	C2—N1—C1—S1	178.3 (3)
Co1—N1—C2—C3	163.2 (3)	C2—N1—C1—N2	0.9 (6)
Co1—N3—C5—S1	−6.0 (5)	C2—C3—C4—N2	0.7 (6)
Co1—N3—C5—C8	168.1 (3)	C2—C3—C4—N6	178.9 (4)
Co1—N3—C6—N4	−164.9 (3)	C4—N2—C1—S1	−176.3 (3)
Cl1—C7—C8—C5	−173.0 (3)	C4—N2—C1—N1	1.5 (6)
S1—C5—C8—C7	172.2 (3)	C5—S1—C1—N1	14.7 (4)
N1—C2—C3—C4	1.8 (6)	C5—S1—C1—N2	−167.4 (3)
N3—C5—C8—C7	−2.5 (6)	C5—N3—C6—N4	6.6 (6)
N4—C7—C8—C5	5.7 (6)	C6—N3—C5—S1	−177.2 (3)
N5—C2—C3—C4	−179.4 (4)	C6—N3—C5—C8	−3.0 (6)
C1—S1—C5—N3	−18.4 (4)	C6—N4—C7—Cl1	175.9 (3)
C1—S1—C5—C8	167.1 (3)	C6—N4—C7—C8	−2.8 (6)
C1—N1—C2—N5	178.5 (4)	C7—N4—C6—N3	−3.8 (6)
C1—N1—C2—C3	−2.5 (5)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N5—H5A $\cdots$ Cl2 ⁱ	0.81 (3)	2.63 (3)	3.385 (4)	156 (5)

N5—H5 <i>B</i> ···Cl3	0.81 (3)	2.53 (3)	3.320 (4)	163 (5)
N6—H6 <i>A</i> ···Cl2 ⁱⁱ	0.81 (3)	2.61 (3)	3.400 (4)	164 (5)
N6—H6 <i>B</i> ···N2 ⁱⁱⁱ	0.81 (3)	2.29 (3)	3.096 (5)	174 (5)

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