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Bis(*N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide) tetrakis(isothiocyanato-κN)cobalt(II), a model compound for the blue color developed in the Scott test

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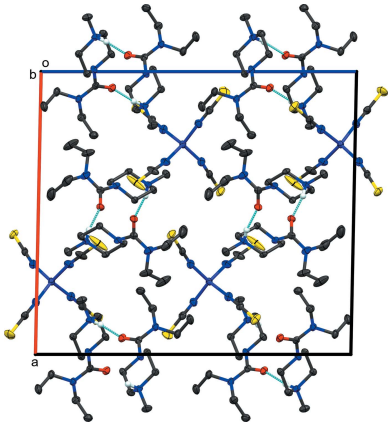
The complex, bis(*N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide) tetrakis(isothiocyanato-κN)cobalt(II) (*N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide = diethylcarbamazine), $(C_{10}H_{22}N_3O)_2[Co(NCS)_4]$, is presented. This complex is a blue precipitate, insoluble in water but soluble in organic solvents, that is formed from the reaction of diethylcarbamazine citrate, a protonated tertiary amine, with cobalt(II) and thiocyanate. This reaction, in the form of the Scott test, is a common presumptive test for cocaine hydrochloride. The known cobalt compound, $[K_2Co(NCS)_4]\cdot 3H_2O$, has a deep-blue coloration due to the tetrahedral $[Co(NCS)_4]^{2-}$ that is also present in the ion pair with bulky amines, and is similar to the color of other tetrahedral cobalt(II) complex ions, such as $[CoCl_4]^{2-}$. The structure is consistent with a previous proposal that a hydrophobic ion pair formed between $[Co(NCS)_4]^{2-}$ and two protonated molecules of cocaine is responsible for the blue hydrophobic products formed by cocaine in the Scott test.

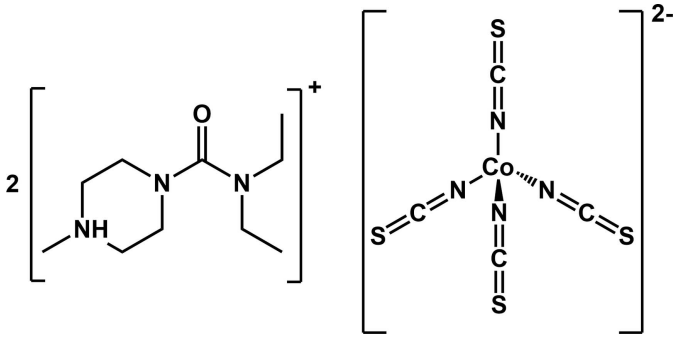
1. Chemical context

In forensics and law enforcement, the Scott test, and modifications to that test (Scott, 1973; Fansello & Higgins, 1986; Tsujikawa *et al.*, 2017), provide identification of tertiary amines from opioids present in a sample. However, there are few reports on the nature of the coloration that is observed during this test, which can vary from powder blue to royal blue, purple, blue–green, or green depending on the identity of the tertiary amine being tested. Oguri and co-workers found that the blue precipitates from cocaine hydrochloride have a 1:2 cobalt:cocaine stoichiometry (Oguri *et al.*, 1995), and IR spectra show the blue precipitates contain one or more thiocyanate units (Morris, 2007). However, the strong blue color is consistent with a tetrahedral Co^{II} species, rather than the octahedral structure postulated by Oguri and co-workers.

As part of our on-going research into detection of functional groups using Paper Analytical Devices (PADs, Weaver *et al.*, 2013; idPADs Lockwood *et al.*, 2020), we sought to understand why tertiary amines give blue precipitates of so many colors in the presence of the Scott reagent. The citrate salt (diethylcarbamazinium citrate; CAS#1642-54-2) of a suitable tertiary amine (diethylcarbamazine; CAS#90-89-1) was selected as a representative tertiary amine. The title compound was prepared by extraction into a CH_2Cl_2 solution from a dried, stoichiometric mixture (1:2) of $K_2[Co(NCS)_4]$



and diethylcarbamazinium citrate that yielded the blue crystals used in this study. The tetrahedral ion $[Co(NCS)_4]^{2-}$ can also be readily formed by disproportionation of the reagent used for the Scott test [the neutral compound $Co(SCN)_2$] in the presence of a suitable amine, as demonstrated in the synthesis for the isothiopendylium tetrakis(isothiocyanato)-cobalt(II) complex (refcode: QUXKOK, Arunkashi *et al.*, 2010), which, like our structure, is an ion pair between two protonated amines and $[Co(NCS)_4]^{2-}$.



This formulation for the ion pair has been proposed in the Scott test literature for cocaine: [Co^{2+} + 4SCN^- +2B: (color red) ⟷ $[Co(SCN)_4)B_2]^{2-}$ (color blue)] (Conceição *et al.*, 2014, in Portugese), and the $[(cocaineH)_2[Co(NCS)_4]$ ion pair features in several flow-injection analysis methods for cocaine, see for example Eisman *et al.* (1992). However, there is still no crystal structure for the Scott test product with cocaine, and only three examples are available for protonated tertiary amine ion pairs with the $[Co(NCS)_4]^{2-}$ dianion.

The Scott test is a three-step sequence of reactions: (1) addition of 2% cobalt thiocyanate in water; (2) addition of 1.2 *M* HCl solution; (3) addition of chloroform. We ascribe the initial blue precipitate in the Scott test to the formation of the ion pair $(amineH)_2[Co(NCS)_4]$. Formation of the ion pair should be a reversible reaction, so when concentrated HCl is added in the second step and it protonates the thiocyanate ions (pK_α for HNCS is 1.1), the tetrahedral cobalt anion falls apart and the blue color vanishes. When chloroform is added in the final step of the Scott test, the hydrophobic ion pair reforms in the organic solvent, turning it blue.

2. Structural commentary

The complex crystallizes with two protonated diethylcarbamazine cations and one tetrakis(isothiocyanato)-cobalt(II) dianion in the asymmetric unit (Fig. 1). The isothiocyanate ligands are bound to the cobalt through their nitrogen atoms, leaving the more bulky and hydrophobic sulfur atoms exposed to the solvent. Protonation of the carbamazines was confirmed by the presence of electron density on the methyl-piperazine nitrogen atoms N6 and N9. The geometry of the carbamazide molecules is unexceptional. The Co^{II} center adopts a near ideal tetrahedral geometry (τ_4 = 0.97; Yang *et al.*, 2007; Table 1) that is located in a general position within the asymmetric unit. In contrast, the cobalt center in the parent compound $K_2[Co(NCS)_4]\cdot 3H_2O$ is located on a twofold screw-axis (space group $P2_12_12$; Drew & Othman, 1975). The τ_4 metric for the parent compound is 0.94 with the largest N—Co—N angle = 114.1 (3)° [in contrast to 112.10 (7)° reported here]. Although this small change should be considered carefully because the Scott test result is a solution phase analysis and here the solid-state structures are compared, it could indicate that the colorimetric response is a change in the tetrahedral ligand field about Co.

Table 1
Selected geometric parameters (Å, °).

Co1—N3	1.9412 (18)	Co1—N1	1.9502 (17)
Co1—N4	1.9451 (18)	Co1—N2	1.9520 (18)
N3—Co1—N4	110.91 (8)	N3—Co1—N2	108.49 (7)
N3—Co1—N1	112.10 (7)	N4—Co1—N2	106.51 (8)
N4—Co1—N1	109.98 (8)	N1—Co1—N2	108.66 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O1^{i}	0.84 (2)	1.86 (2)	2.691 (2)	169 (2)
N9—H9···O2^{ii}	0.88 (2)	1.82 (2)	2.694 (2)	172 (2)

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

3. Supramolecular features

Both protonated tertiary amine nitrogen atoms are involved in intermolecular hydrogen bonding with amide oxygen atoms of an identical molecule related by the screw-axis along the *b*-axis, resulting in mono-periodic chains of each amide along the *b*-axis direction (Fig. 2). Thus, N6 forms a hydrogen bond to O1^{i} and N9 to O2^{ii} [symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; see Table 2 for details]. Both chains are identified as having graph-set motif $C_1^1(7)$ (Etter *et al.*, 1990).

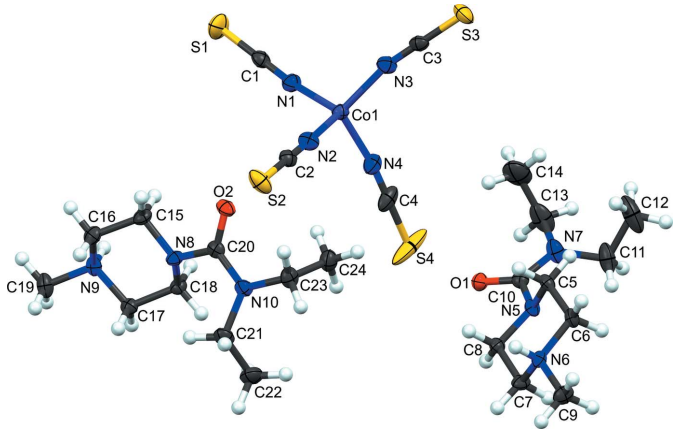


Figure 1
Molecular structure of bis(diethylcarbamazide) tetrakis(isothiocyanato)-cobalt(II). Atomic displacement ellipsoids depicted at the 50% probability level. Hydrogen atoms are shown as spheres of an arbitrary radius.

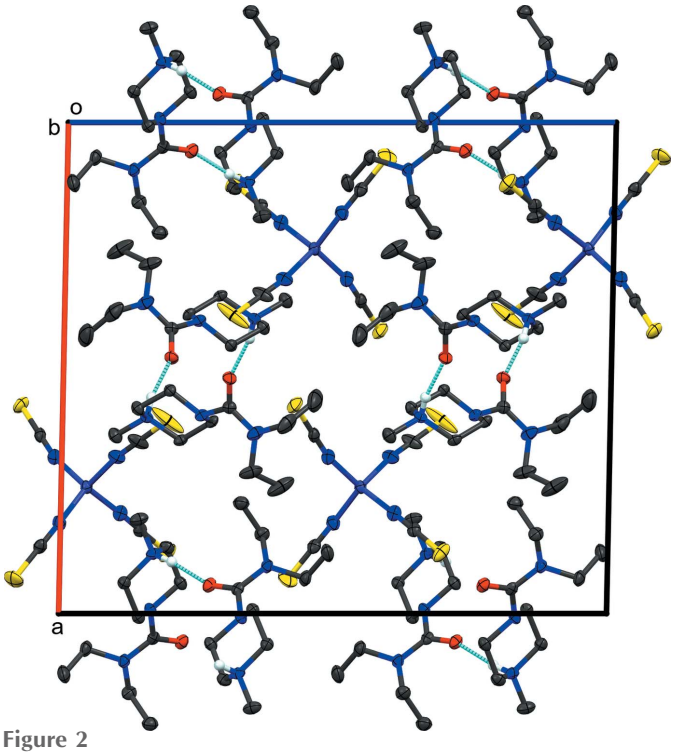


Figure 2
Packing diagram of bis(diethylcarbamazide) tetrakis(isothiocyanato)-cobalt(II) viewed along the *b*-axis. Hydrogen atoms, except for those involved in hydrogen bonding, have been omitted for clarity. Blue dashed lines represent hydrogen-bonding interactions.

4. Database survey

The core structure of *N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide is only reported in five instances in the Cambridge Structural Database (CSD, v 5.43, update 4, November 2022; Groom *et al.*, 2016). One is a diphenyl morpholine derivative, [4-(diphenylmethyl)-piperazin-1-yl](morpholin-4-yl)methanone (refcode: IDOVAB, Kumar *et al.*, 2017). The remaining four reported structures are a series of citrates reported by da Silva and co-workers (refcodes: QURWOQ, QURWOQ01, QURWOQ02, and QURWOQ03; da Silva *et al.*, 2010). Diethylcarbamazide citrate is used widely in the treatment of filariasis. Comparing the diethylcarbamazide molecules reported herein with those with citrate counter-ions reported by da Silva, the structures are essentially identical. Two of da Silva's structures have some ethyl chain disorder that is the only significant difference compared with the structure reported here. Tetrakis(isothiocyanato)-cobalt(II) is reported in over 200 structures. At the intersection of (isothiocyanto)cobalt and tertiary amines there are five structures. Two of these structures contain hexakis(isothiocyanato)cobalt (refcode: ILOXEP, Makhlouf, 2021; KIPYUD, Mali *et al.*, 1991) and are not pertinent to the discussion. The remaining three compounds {QUXKOK, [*N*,*N*-dimethyl-1-(10*H*-pyrido[3,2-*b*][1,4]benzothiazin-10-yl)-propan-2-aminium] (isothiopendylium), Arunkashi *et al.*, 2010; XIXQUT, [trimethylammonium], Jie *et al.*, 2018; YEPHIK, [2-diethylamino-*N*-(2,6-dimethylphenyl)acetamide] (lignocainium), Qayyas *et al.*, 1994} contain a tetrakis(isothiocyanato)cobalt(II) anion and associated tertiary amine cation. Bond angles about the cobalt centers in these three structures are similar to those reported here (range for angles about Co is 104.78 to 114.05°).

Table 3
Experimental details.

Crystal data	
Chemical formula	$(C_{10}H_{22}N_3O)_2[Co(NCS)_4]$
M_r	691.86
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	17.915 (2), 9.8192 (13), 19.954 (3)
β (°)	91.150 (2)
V (Å^3)	3509.4 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.76
Crystal size (mm)	0.28 × 0.07 × 0.06
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.810, 0.979
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	66480, 8799, 6514
R_{int}	0.052
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.087, 1.01
No. of reflections	8799
No. of parameters	384
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.98, −1.11

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

$K_2[Co(NCS)_4]$ was prepared by the metathesis of $Co(NO_3)_2$ (3.00 g, 16.4 mmol) and K(SCN) (3.88 g, 39.9 mmol) in 20 mL of water and allowed to dry. Dark-blue crystals were harvested for subsequent reactions; note: upon dissolution in water the solution is pink. $K_2[Co(NCS)_4]$ and diethylcarbamazide citrate were mixed in a stoichiometric (1:2) ratio in water and allowed to dry. $CHCl_3$ or CH_2Cl_2 was added to extract the blue complex. Crystals were grown from the CH_2Cl_2 extract by vapor diffusion of hexane at 277 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bonded to tertiary amine nitrogen atoms (N6, N9) were refined freely. All other hydrogen atoms were included in geometrically calculated positions with C—H bond distances constrained to 0.98 Å for aromatic and methylene and 0.99 Å for methyl hydrogen atoms with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl and $1.2U_{eq}(C)$ for aromatic and methylene H atoms.

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References

Arunkashi, H. K., Jeyaseelan, S., Vepuri, S. B., Revanasiddappa, H. D. & Devarajegowda, H. C. (2010). *Acta Cryst.* E**66**, m772–m773.
Bruker (2018). *APEX3* and *SAINT*, Bruker–Nonius AXS Inc. Madison, Wisconsin, USA.
Conceição, V. N., Souza, L. M., Merlo, B. B., Filgueiras, P. R., Poppi, R. J. & Romão, W. (2014). *Quím. Nova* **37**(9), 1538–1544.
Drew, M. G. B. & Hamid bin Othman, A. (1975). *Acta Cryst.* B**31**, 613–614.
Eisman, M., Gallego, M. & Valcárcel, M. (1992). *Anal. Chem.* **64**, 1509–1512.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Fansello, J. & Higgins, P. (1986). *Microgram.* **19**, 137–138.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Jie, Y., Yuan, H., YouQuan, Z., Ting, F., Fan, H., Qian, K. & Ye, Y.-H. (2018). *Z. Naturforsch.* **73**, 571–575.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Kumar, C. S. A., Naveen, S., Prasad, S. B. B., Gowda, N. S. L. & Lokanath, N. K. (2017). *J. Appl. Chem.* **6**, 274–281.
Lockwood, T. E., Leong, T. X., Bliese, S. L., Helmke, A., Richard, A., Merga, G., Rorabeck, J. & Lieberman, M. (2020). *J. Forensic Sci.* **65**, 1289–1297.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Makhlouf, J. (2021). *CSD Communication* (refcode ILOXEP, CCDC2061180). CCDC, Cambridge, England.
Mali, T. N., Hancock, R. D., Boeyens, J. C. A. & Oosthuizen, E. L. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1161–1163.
Morris, J. A. (2007). *J. Forensic Sci.* **52**, 84–87.
Oguri, K., Wada, S., Eto, S. & Yamada, H. (1995). *Eisei Kagaku*, **41**, 274–279.
Qayyas, N. N. A., Sridhar, M. A., Indria, A. & Prasad, J. S. (1994). *Z. Kristallogr. Cryst. Mater.* **209**(11), 918–919.
Scott, L. J. (1973). *Microgram.* **6**, 179–181.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Silva, C. C. P. da, Martins, F. T., Honorato, S. B., Boechat, N., Ayala, A. P. & Ellena, J. (2010). *Cryst. Growth Des.* **10**, 3094–3101.
Tsujikawa, K., Iwata, Y. T., Segawa, H., Yamamuro, T., Kuwayama, K., Kanamori, T. & Inoue, H. (2017). *Forensic Sci. Int.* **270**, 267–274.
Weaver, A. A., Reiser, H., Barstis, T., Benvenuti, M., Ghosh, D., Hunckler, M., Joy, B., Koenig, L., Raddell, K. & Lieberman, M. (2013). *Anal. Chem.* **85**, 6453–6460.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yang, L., Powell, D. R. & Houser, R. P. (2007). *Dalton Trans.* pp. 955–964.

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Bis(*N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide) tetrakis(isothiocyanato-κ*N*)cobalt(II), a model compound for the blue color developed in the Scott test

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Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(*N*,*N*-diethyl-4-methyl-4-piperazine-1-carboxamide) tetrakis(isothiocyanato-κ*N*)cobalt(II)

Crystal data

$(C_{10}H_{22}N_3O)_2[Co(NCS)_4]$
M_r = 691.86
Monoclinic, $P2_1/c$
a = 17.915 (2) Å
b = 9.8192 (13) Å
c = 19.954 (3) Å
β = 91.150 (2)°
V = 3509.4 (8) Å^3
Z = 4
$F(000)$ = 1460
D_x = 1.309 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9913 reflections
θ = 2.3–27.6°
μ = 0.76 mm^{-1}
T = 120 K
Rod, blue
0.28 × 0.07 × 0.06 mm

Data collection

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.33 pixels mm^{-1}
combination of ω and φ–scans
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)
T_{min} = 0.810, T_{max} = 0.979
66480 measured reflections
8799 independent reflections
6514 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 28.4°, θ_{min} = 1.1°
h = −23→23
k = −13→13
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.087
S = 1.01
8799 reflections
384 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 2.9287P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −1.11 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.74254 (2)	0.61672 (3)	0.54618 (2)	0.02168 (7)
S1	0.92990 (4)	0.81311 (8)	0.41695 (4)	0.05019 (18)
S2	0.87654 (4)	0.32929 (6)	0.69618 (3)	0.03974 (15)
S3	0.57552 (3)	0.33888 (7)	0.42353 (3)	0.03850 (14)
S4	0.60666 (5)	0.89379 (7)	0.69206 (6)	0.0898 (4)
N1	0.81550 (10)	0.72430 (18)	0.49788 (8)	0.0287 (4)
N2	0.79572 (10)	0.49630 (18)	0.60861 (9)	0.0296 (4)
N3	0.68112 (10)	0.50601 (18)	0.48628 (8)	0.0286 (4)
N4	0.68106 (10)	0.73551 (18)	0.60020 (9)	0.0313 (4)
C1	0.86334 (12)	0.7621 (2)	0.46387 (10)	0.0264 (4)
C2	0.83000 (11)	0.4275 (2)	0.64557 (10)	0.0247 (4)
C3	0.63674 (12)	0.4369 (2)	0.45962 (9)	0.0249 (4)
C4	0.64989 (13)	0.8006 (2)	0.63879 (13)	0.0373 (6)
O1	0.47917 (7)	1.15381 (14)	0.69673 (7)	0.0262 (3)
N5	0.40377 (9)	0.99660 (16)	0.74649 (8)	0.0205 (3)
N6	0.39973 (9)	0.78750 (17)	0.84633 (8)	0.0209 (3)
H6	0.4399 (12)	0.747 (2)	0.8383 (10)	0.022 (6)*
N7	0.36711 (10)	1.10644 (18)	0.64724 (9)	0.0324 (4)
C5	0.39077 (11)	0.85401 (18)	0.72708 (9)	0.0210 (4)
H5A	0.438946	0.809565	0.717291	0.025*
H5B	0.358850	0.850411	0.686039	0.025*
C6	0.35303 (10)	0.7795 (2)	0.78338 (9)	0.0222 (4)
H6A	0.303459	0.820433	0.791130	0.027*
H6B	0.345499	0.682859	0.770736	0.027*
C7	0.41778 (11)	0.9324 (2)	0.86332 (10)	0.0241 (4)
H7A	0.451831	0.935096	0.902995	0.029*
H7B	0.371368	0.981171	0.874750	0.029*
C8	0.45436 (11)	1.0032 (2)	0.80495 (9)	0.0216 (4)
H8A	0.464916	1.099404	0.816562	0.026*
H8B	0.502182	0.957921	0.794761	0.026*
C9	0.36244 (12)	0.7175 (2)	0.90305 (10)	0.0304 (5)
H9A	0.393790	0.725334	0.943679	0.046*
H9B	0.355143	0.621148	0.891989	0.046*
H9C	0.313896	0.760209	0.910702	0.046*
C10	0.41985 (11)	1.08939 (19)	0.69569 (10)	0.0223 (4)
C11	0.28776 (13)	1.0721 (3)	0.65439 (14)	0.0458 (6)
H11A	0.258149	1.157241	0.654449	0.055*
H11B	0.280949	1.026491	0.698088	0.055*
C12	0.25841 (16)	0.9804 (3)	0.59917 (17)	0.0664 (9)

H12A	0.260202	1.028600	0.556220	0.100*
H12B	0.206713	0.954935	0.608292	0.100*
H12C	0.289270	0.898163	0.597135	0.100*
C13	0.38615 (16)	1.1942 (3)	0.59024 (14)	0.0519 (7)
H13A	0.413605	1.275130	0.607109	0.062*
H13B	0.339571	1.226213	0.567837	0.062*
C14	0.43331 (19)	1.1209 (4)	0.53983 (14)	0.0682 (9)
H14A	0.446433	1.183855	0.503827	0.102*
H14B	0.405125	1.043954	0.520909	0.102*
H14C	0.478997	1.087235	0.562009	0.102*
O2	0.94210 (8)	0.06408 (14)	0.77411 (7)	0.0263 (3)
N8	1.00777 (9)	0.22499 (16)	0.83271 (8)	0.0212 (3)
N9	1.12181 (9)	0.42920 (17)	0.82969 (9)	0.0230 (3)
H9	1.1052 (12)	0.478 (2)	0.7954 (11)	0.034 (6)*
N10	0.90345 (9)	0.11786 (17)	0.87878 (8)	0.0240 (3)
C15	1.06216 (11)	0.2245 (2)	0.77881 (10)	0.0249 (4)
H15A	1.042531	0.277347	0.740055	0.030*
H15B	1.071278	0.129933	0.763850	0.030*
C16	1.13451 (11)	0.2875 (2)	0.80479 (10)	0.0261 (4)
H16A	1.155428	0.230933	0.841675	0.031*
H16B	1.171222	0.289546	0.768375	0.031*
C17	1.06253 (10)	0.4300 (2)	0.88160 (9)	0.0229 (4)
H17A	1.051975	0.525004	0.895086	0.028*
H17B	1.080422	0.379663	0.921790	0.028*
C18	0.99185 (10)	0.36465 (18)	0.85434 (9)	0.0209 (4)
H18A	0.953590	0.363374	0.889451	0.025*
H18B	0.972047	0.418252	0.815905	0.025*
C19	1.19218 (11)	0.4913 (2)	0.85676 (12)	0.0329 (5)
H19A	1.183296	0.587218	0.867644	0.049*
H19B	1.231081	0.485059	0.823061	0.049*
H19C	1.208379	0.442525	0.897345	0.049*
C20	0.94966 (10)	0.13172 (18)	0.82610 (9)	0.0209 (4)
C21	0.92829 (12)	0.1378 (2)	0.94905 (10)	0.0303 (5)
H21A	0.978919	0.178300	0.949711	0.036*
H21B	0.931594	0.048027	0.971455	0.036*
C22	0.87648 (14)	0.2293 (3)	0.98833 (11)	0.0408 (6)
H22A	0.876818	0.321136	0.969135	0.061*
H22B	0.893574	0.233173	1.035258	0.061*
H22C	0.825651	0.192474	0.985933	0.061*
C23	0.83827 (11)	0.0288 (2)	0.86836 (11)	0.0291 (4)
H23A	0.819629	0.000020	0.912537	0.035*
H23B	0.853961	−0.054001	0.844096	0.035*
C24	0.77536 (12)	0.0968 (2)	0.82916 (11)	0.0334 (5)
H24A	0.793927	0.129085	0.786114	0.050*
H24B	0.756463	0.174142	0.854792	0.050*
H24C	0.734967	0.031080	0.821181	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02440 (13)	0.02027 (13)	0.02043 (13)	−0.00148 (11)	0.00194 (10)	0.00012 (11)
S1	0.0401 (4)	0.0601 (4)	0.0510 (4)	−0.0233 (3)	0.0147 (3)	0.0044 (3)
S2	0.0480 (4)	0.0311 (3)	0.0393 (3)	−0.0055 (3)	−0.0194 (3)	0.0092 (2)
S3	0.0379 (3)	0.0448 (3)	0.0323 (3)	−0.0053 (3)	−0.0132 (2)	−0.0080 (3)
S4	0.0949 (6)	0.0321 (4)	0.1462 (9)	−0.0231 (4)	0.0978 (7)	−0.0344 (5)
N1	0.0318 (10)	0.0283 (9)	0.0260 (9)	−0.0050 (8)	0.0033 (7)	0.0005 (7)
N2	0.0343 (10)	0.0263 (9)	0.0282 (9)	0.0004 (8)	−0.0015 (8)	−0.0002 (7)
N3	0.0345 (10)	0.0271 (9)	0.0242 (9)	−0.0035 (8)	−0.0002 (7)	0.0006 (7)
N4	0.0283 (9)	0.0266 (9)	0.0393 (10)	−0.0023 (8)	0.0067 (8)	−0.0045 (8)
C1	0.0304 (11)	0.0226 (10)	0.0261 (10)	−0.0058 (8)	−0.0033 (9)	−0.0026 (8)
C2	0.0282 (10)	0.0213 (10)	0.0247 (10)	−0.0065 (8)	−0.0007 (8)	−0.0027 (8)
C3	0.0307 (11)	0.0263 (10)	0.0177 (9)	0.0046 (9)	0.0005 (8)	0.0025 (8)
C4	0.0333 (12)	0.0190 (10)	0.0604 (15)	−0.0071 (9)	0.0214 (11)	−0.0025 (10)
O1	0.0246 (7)	0.0281 (7)	0.0261 (7)	−0.0076 (6)	0.0031 (6)	0.0000 (6)
N5	0.0212 (8)	0.0165 (8)	0.0238 (8)	−0.0024 (6)	−0.0023 (6)	−0.0015 (6)
N6	0.0189 (8)	0.0209 (8)	0.0229 (8)	0.0017 (7)	0.0025 (6)	−0.0008 (6)
N7	0.0294 (9)	0.0268 (9)	0.0406 (10)	−0.0038 (8)	−0.0102 (8)	0.0111 (8)
C5	0.0225 (9)	0.0174 (9)	0.0229 (9)	−0.0010 (7)	−0.0062 (7)	−0.0025 (7)
C6	0.0188 (9)	0.0196 (9)	0.0281 (10)	−0.0024 (7)	−0.0046 (8)	0.0006 (8)
C7	0.0284 (10)	0.0205 (9)	0.0236 (10)	−0.0014 (8)	0.0044 (8)	−0.0047 (8)
C8	0.0221 (9)	0.0210 (9)	0.0216 (9)	−0.0037 (8)	0.0004 (7)	−0.0038 (7)
C9	0.0344 (12)	0.0283 (11)	0.0287 (11)	−0.0033 (9)	0.0071 (9)	0.0054 (9)
C10	0.0232 (10)	0.0176 (9)	0.0261 (10)	0.0009 (7)	0.0010 (8)	−0.0018 (7)
C11	0.0265 (12)	0.0362 (13)	0.0738 (18)	−0.0012 (10)	−0.0165 (12)	0.0140 (13)
C12	0.0529 (17)	0.0469 (17)	0.097 (2)	−0.0115 (14)	−0.0454 (17)	0.0176 (16)
C13	0.0565 (17)	0.0458 (16)	0.0523 (16)	−0.0158 (13)	−0.0244 (13)	0.0284 (13)
C14	0.076 (2)	0.094 (3)	0.0339 (14)	−0.0269 (19)	−0.0073 (14)	0.0207 (16)
O2	0.0295 (7)	0.0231 (7)	0.0260 (7)	0.0027 (6)	−0.0047 (6)	−0.0068 (6)
N8	0.0246 (8)	0.0180 (8)	0.0212 (8)	−0.0009 (6)	0.0046 (6)	−0.0029 (6)
N9	0.0203 (8)	0.0206 (8)	0.0280 (9)	0.0013 (7)	−0.0026 (7)	0.0067 (7)
N10	0.0270 (8)	0.0249 (8)	0.0201 (8)	−0.0042 (7)	−0.0019 (6)	0.0050 (7)
C15	0.0279 (10)	0.0222 (10)	0.0250 (10)	0.0027 (8)	0.0060 (8)	−0.0032 (8)
C16	0.0244 (10)	0.0238 (10)	0.0304 (11)	0.0050 (8)	0.0039 (8)	0.0006 (8)
C17	0.0244 (10)	0.0211 (9)	0.0233 (9)	0.0021 (8)	−0.0004 (8)	−0.0011 (8)
C18	0.0227 (9)	0.0177 (9)	0.0225 (9)	0.0019 (7)	0.0018 (7)	−0.0005 (7)
C19	0.0230 (10)	0.0282 (11)	0.0472 (13)	−0.0028 (9)	−0.0060 (9)	0.0044 (10)
C20	0.0245 (9)	0.0157 (9)	0.0225 (9)	0.0045 (7)	−0.0031 (7)	0.0040 (7)
C21	0.0360 (12)	0.0347 (12)	0.0201 (10)	−0.0050 (9)	−0.0039 (8)	0.0082 (8)
C22	0.0464 (14)	0.0538 (15)	0.0227 (11)	−0.0084 (12)	0.0076 (10)	0.0005 (10)
C23	0.0290 (11)	0.0260 (11)	0.0322 (11)	−0.0061 (9)	−0.0015 (9)	0.0072 (9)
C24	0.0257 (11)	0.0375 (13)	0.0369 (12)	−0.0022 (9)	0.0011 (9)	0.0055 (10)

Geometric parameters (Å, º)

Co1—N3	1.9412 (18)	C13—C14	1.509 (4)
Co1—N4	1.9451 (18)	C13—H13A	0.9900
Co1—N1	1.9502 (17)	C13—H13B	0.9900
Co1—N2	1.9520 (18)	C14—H14A	0.9800
S1—C1	1.611 (2)	C14—H14B	0.9800
S2—C2	1.616 (2)	C14—H14C	0.9800
S3—C3	1.618 (2)	O2—C20	1.237 (2)
S4—C4	1.613 (2)	N8—C20	1.391 (2)
N1—C1	1.165 (3)	N8—C15	1.466 (2)
N2—C2	1.166 (3)	N8—C18	1.467 (2)
N3—C3	1.165 (3)	N9—C19	1.492 (3)
N4—C4	1.153 (3)	N9—C16	1.496 (3)
O1—C10	1.236 (2)	N9—C17	1.498 (2)
N5—C10	1.397 (2)	N9—H9	0.88 (2)
N5—C8	1.464 (2)	N10—C20	1.358 (2)
N5—C5	1.470 (2)	N10—C23	1.470 (3)
N6—C9	1.493 (2)	N10—C21	1.476 (2)
N6—C7	1.497 (2)	C15—C16	1.518 (3)
N6—C6	1.497 (2)	C15—H15A	0.9900
N6—H6	0.84 (2)	C15—H15B	0.9900
N7—C10	1.349 (3)	C16—H16A	0.9900
N7—C11	1.471 (3)	C16—H16B	0.9900
N7—C13	1.472 (3)	C17—C18	1.511 (3)
C5—C6	1.512 (3)	C17—H17A	0.9900
C5—H5A	0.9900	C17—H17B	0.9900
C5—H5B	0.9900	C18—H18A	0.9900
C6—H6A	0.9900	C18—H18B	0.9900
C6—H6B	0.9900	C19—H19A	0.9800
C7—C8	1.516 (3)	C19—H19B	0.9800
C7—H7A	0.9900	C19—H19C	0.9800
C7—H7B	0.9900	C21—C22	1.520 (3)
C8—H8A	0.9900	C21—H21A	0.9900
C8—H8B	0.9900	C21—H21B	0.9900
C9—H9A	0.9800	C22—H22A	0.9800
C9—H9B	0.9800	C22—H22B	0.9800
C9—H9C	0.9800	C22—H22C	0.9800
C11—C12	1.509 (4)	C23—C24	1.514 (3)
C11—H11A	0.9900	C23—H23A	0.9900
C11—H11B	0.9900	C23—H23B	0.9900
C12—H12A	0.9800	C24—H24A	0.9800
C12—H12B	0.9800	C24—H24B	0.9800
C12—H12C	0.9800	C24—H24C	0.9800
N3—Co1—N4	110.91 (8)	H13A—C13—H13B	107.9
N3—Co1—N1	112.10 (7)	C13—C14—H14A	109.5
N4—Co1—N1	109.98 (8)	C13—C14—H14B	109.5

N3—Co1—N2	108.49 (7)	H14A—C14—H14B	109.5
N4—Co1—N2	106.51 (8)	C13—C14—H14C	109.5
N1—Co1—N2	108.66 (8)	H14A—C14—H14C	109.5
C1—N1—Co1	165.66 (17)	H14B—C14—H14C	109.5
C2—N2—Co1	177.29 (17)	C20—N8—C15	115.83 (15)
C3—N3—Co1	168.53 (16)	C20—N8—C18	119.59 (15)
C4—N4—Co1	171.6 (2)	C15—N8—C18	110.79 (15)
N1—C1—S1	179.5 (2)	C19—N9—C16	111.56 (16)
N2—C2—S2	178.74 (19)	C19—N9—C17	110.67 (16)
N3—C3—S3	179.0 (2)	C16—N9—C17	110.44 (15)
N4—C4—S4	179.1 (2)	C19—N9—H9	109.3 (15)
C10—N5—C8	114.57 (15)	C16—N9—H9	107.2 (15)
C10—N5—C5	117.62 (15)	C17—N9—H9	107.5 (15)
C8—N5—C5	110.14 (14)	C20—N10—C23	116.42 (16)
C9—N6—C7	111.33 (15)	C20—N10—C21	123.05 (16)
C9—N6—C6	111.14 (15)	C23—N10—C21	115.91 (16)
C7—N6—C6	110.78 (15)	N8—C15—C16	108.90 (16)
C9—N6—H6	108.9 (14)	N8—C15—H15A	109.9
C7—N6—H6	108.3 (15)	C16—C15—H15A	109.9
C6—N6—H6	106.3 (14)	N8—C15—H15B	109.9
C10—N7—C11	124.52 (19)	C16—C15—H15B	109.9
C10—N7—C13	117.16 (18)	H15A—C15—H15B	108.3
C11—N7—C13	116.64 (19)	N9—C16—C15	110.97 (16)
N5—C5—C6	109.64 (15)	N9—C16—H16A	109.4
N5—C5—H5A	109.7	C15—C16—H16A	109.4
C6—C5—H5A	109.7	N9—C16—H16B	109.4
N5—C5—H5B	109.7	C15—C16—H16B	109.4
C6—C5—H5B	109.7	H16A—C16—H16B	108.0
H5A—C5—H5B	108.2	N9—C17—C18	110.44 (15)
N6—C6—C5	110.31 (15)	N9—C17—H17A	109.6
N6—C6—H6A	109.6	C18—C17—H17A	109.6
C5—C6—H6A	109.6	N9—C17—H17B	109.6
N6—C6—H6B	109.6	C18—C17—H17B	109.6
C5—C6—H6B	109.6	H17A—C17—H17B	108.1
H6A—C6—H6B	108.1	N8—C18—C17	109.66 (15)
N6—C7—C8	110.88 (15)	N8—C18—H18A	109.7
N6—C7—H7A	109.5	C17—C18—H18A	109.7
C8—C7—H7A	109.5	N8—C18—H18B	109.7
N6—C7—H7B	109.5	C17—C18—H18B	109.7
C8—C7—H7B	109.5	H18A—C18—H18B	108.2
H7A—C7—H7B	108.1	N9—C19—H19A	109.5
N5—C8—C7	108.76 (15)	N9—C19—H19B	109.5
N5—C8—H8A	109.9	H19A—C19—H19B	109.5
C7—C8—H8A	109.9	N9—C19—H19C	109.5
N5—C8—H8B	109.9	H19A—C19—H19C	109.5
C7—C8—H8B	109.9	H19B—C19—H19C	109.5
H8A—C8—H8B	108.3	O2—C20—N10	122.49 (18)
N6—C9—H9A	109.5	O2—C20—N8	120.16 (17)

N6—C9—H9B	109.5	N10—C20—N8	117.35 (16)
H9A—C9—H9B	109.5	N10—C21—C22	113.13 (18)
N6—C9—H9C	109.5	N10—C21—H21A	109.0
H9A—C9—H9C	109.5	C22—C21—H21A	109.0
H9B—C9—H9C	109.5	N10—C21—H21B	109.0
O1—C10—N7	122.55 (18)	C22—C21—H21B	109.0
O1—C10—N5	120.73 (17)	H21A—C21—H21B	107.8
N7—C10—N5	116.70 (17)	C21—C22—H22A	109.5
N7—C11—C12	112.9 (2)	C21—C22—H22B	109.5
N7—C11—H11A	109.0	H22A—C22—H22B	109.5
C12—C11—H11A	109.0	C21—C22—H22C	109.5
N7—C11—H11B	109.0	H22A—C22—H22C	109.5
C12—C11—H11B	109.0	H22B—C22—H22C	109.5
H11A—C11—H11B	107.8	N10—C23—C24	113.06 (17)
C11—C12—H12A	109.5	N10—C23—H23A	109.0
C11—C12—H12B	109.5	C24—C23—H23A	109.0
H12A—C12—H12B	109.5	N10—C23—H23B	109.0
C11—C12—H12C	109.5	C24—C23—H23B	109.0
H12A—C12—H12C	109.5	H23A—C23—H23B	107.8
H12B—C12—H12C	109.5	C23—C24—H24A	109.5
N7—C13—C14	112.2 (2)	C23—C24—H24B	109.5
N7—C13—H13A	109.2	H24A—C24—H24B	109.5
C14—C13—H13A	109.2	C23—C24—H24C	109.5
N7—C13—H13B	109.2	H24A—C24—H24C	109.5
C14—C13—H13B	109.2	H24B—C24—H24C	109.5

C10—N5—C5—C6	−163.66 (16)	C20—N8—C15—C16	−158.44 (16)
C8—N5—C5—C6	62.57 (19)	C18—N8—C15—C16	61.2 (2)
C9—N6—C6—C5	178.50 (16)	C19—N9—C16—C15	178.76 (17)
C7—N6—C6—C5	54.2 (2)	C17—N9—C16—C15	55.2 (2)
N5—C5—C6—N6	−57.8 (2)	N8—C15—C16—N9	−57.8 (2)
C9—N6—C7—C8	−178.98 (16)	C19—N9—C17—C18	−178.96 (16)
C6—N6—C7—C8	−54.8 (2)	C16—N9—C17—C18	−54.9 (2)
C10—N5—C8—C7	162.42 (16)	C20—N8—C18—C17	159.67 (16)
C5—N5—C8—C7	−62.29 (19)	C15—N8—C18—C17	−61.6 (2)
N6—C7—C8—N5	58.3 (2)	N9—C17—C18—N8	57.8 (2)
C11—N7—C10—O1	−157.7 (2)	C23—N10—C20—O2	−6.6 (3)
C13—N7—C10—O1	7.0 (3)	C21—N10—C20—O2	148.25 (19)
C11—N7—C10—N5	20.8 (3)	C23—N10—C20—N8	174.26 (16)
C13—N7—C10—N5	−174.5 (2)	C21—N10—C20—N8	−30.9 (3)
C8—N5—C10—O1	11.3 (2)	C15—N8—C20—O2	−6.9 (3)
C5—N5—C10—O1	−120.47 (19)	C18—N8—C20—O2	129.85 (18)
C8—N5—C10—N7	−167.22 (17)	C15—N8—C20—N10	172.25 (16)
C5—N5—C10—N7	61.0 (2)	C18—N8—C20—N10	−51.0 (2)
C10—N7—C11—C12	−127.1 (2)	C20—N10—C21—C22	131.8 (2)
C13—N7—C11—C12	68.1 (3)	C23—N10—C21—C22	−73.2 (2)
C10—N7—C13—C14	79.7 (3)	C20—N10—C23—C24	−78.8 (2)
C11—N7—C13—C14	−114.4 (3)	C21—N10—C23—C24	124.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O1^{i}	0.84 (2)	1.86 (2)	2.691 (2)	169 (2)
N9—H9···O2^{ii}	0.88 (2)	1.82 (2)	2.694 (2)	172 (2)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+2, *y*+1/2, −*z*+3/2.