research communications

Synthesis, molecular and crystal structure of [(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$_2$[RuBr$_6$]Br$_2$·3H$_2$O

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The title compound, bis[dithiobis(formamidinium)] hexabromidoruthenium dibromide trihydrate, [(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$_2$[RuBr$_6$]Br$_2$·3H$_2$O, crystallizes in the orthorhombic system, space group $Cmcm$, $Z = 4$. The [RuBr$_6$]$^{2-}$ anionic complex has an octahedral structure. The Ru—Br distances fall in the range 2.4779 (4)–2.4890 (4) Å. The S—S and C—S distances are 2.0282 (12) and 1.783 (2) Å, respectively. The H$_2$O molecules, Br$^-$ ions, and NH$_2$ groups of the cation are linked by hydrogen bonds. The conformation of the cation is consolidated by intramolecular O—H···Br, O—H···O, N—H···Br and N—H···O hydrogen bonds. The [(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$^{2+}$ cations form a hydrogen-bonded system involving the Br$^-$ ions and the water molecules. Two Br$^-$ anions form four hydrogen bonds, each with the NH$_2$ groups of two cations, thus linking the cations into a ring. The rings are connected by water molecules, forming N—H···O—H···Br hydrogen bonds.

1. Chemical context

Oxidation of thiocarbamide in an acidic medium results in the αα′-(dithiobisformamidinium) cation {[(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$^{2+}$ or [S$_2$C$_2$(NH$_2$)$_4$]$^{2+}$ in a simplified form; Preisler & Berger, 1947}. There are only a few examples of compounds containing [S$_2$C$_2$(NH$_2$)$_4$]$^{2+}$ cations described in the literature. For example, direct interaction of compounds with [S$_2$C$_2$(NH$_2$)$_4$]Cl$_2$ in concentrated hydrochloric acid produced [S$_2$C$_2$(NH$_2$)$_4$][MCl$_4$], M = Cu, Co, Zn, Hg (Golovnev et al., 2013), [S$_2$C$_2$(NH$_2$)$_4$]$_2$[Hg$_2$Cl$_8$] (Vasiliev et al., 2013) and [S$_2$C$_2$(NH$_2$)$_4$]$_2$[Os^{IV}Cl$_6$]Cl$_2$·3H$_2$O (Rudnitskaya et al., 2019), while changing the reaction medium to concentrated hydrobromic acid resulted in the formation of [S$_2$C$_2$(NH$_2$)$_4$][HgBr$_4$] (Golovnev et al., 2013).

From the point of view of synthetic coordination chemistry, the reactions of rhenium and osmium complexes with thiocarbamide are of interest. These reactions led to compounds with an outer sphere dithiobisformamidinium cation. Thus, the interaction of ReO$_4^-$ with thiocarbamide (tu) in hydrochloric acid allows the preparation of complexes [S$_2$C$_2$(NH$_2$)$_4$][ReCl$_4$(H$_2$O)O], [S$_2$C$_2$(NH$_2$)$_4$]$_2$[ReCl$_5$(H$_2$O)]Cl$_3$·2H$_2$O and [S$_2$C$_2$(NH$_2$)$_4$]$_2$[ReCl$_5$(tu)]Cl (Lis, 1979, 1980; Lis & Starynowicz, 1985). In this case, oxidation of thiourea (hereinafter, ***tu***) occurs by rhenium(VII). When K$_2$[ReCl$_6$] reacts with ***tu*** in dilute HCl, thiocarbamide oxidation occurs under the influence of atmospheric oxygen, giving [S$_2$C$_2$(NH$_2$)$_4$]$_2$[ReCl$_6$]Cl$_2$·3H$_2$O (Lis & Starynowicz, 1985). Similar complexes
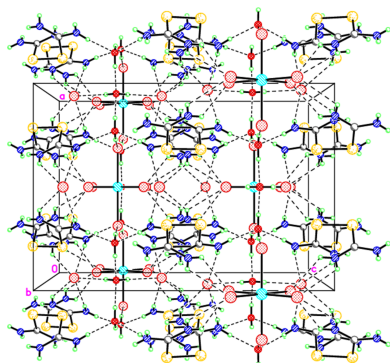
$[S_2C_2(NH_2)_4]_2[OsX_6]X_2 \cdot 3H_2O$ where X = Cl, Br were obtained by the reaction of $H_2[OsX_6]$ and ***tu*** in concentrated HCl and HBr, respectively. In the aforementioned case, thiocarbamide was oxidized by osmium(IV) (Rudnitskaya *et al.*, 2008, 2019). The molecular and crystal structures of the rhenium and osmium complexes discussed above were established by X-ray diffraction. The interaction of $K_4[Ru_2OCl_{10}]$ with α,α'-(dithiobisformamidinium) chloride forms the unique ruthenium(III) compound $[Ru_2(tu)_3Cl_6]\cdot$ $2H_2O$, containing three ***tu*** bridging molecules (Rudnitskaya *et al.*, 2017*a*). The structure of $[Cl_3Ru(tu)_3RuCl_3]$ will be published elsewhere.
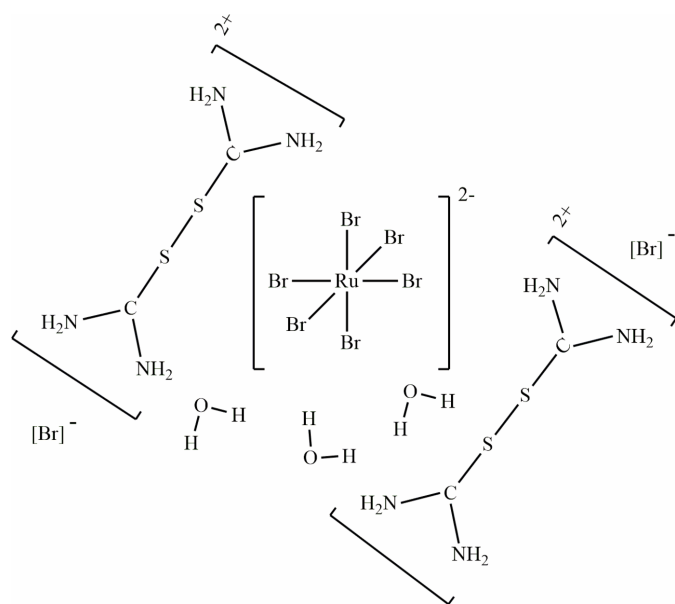
This study aimed to investigate the interaction between ruthenium compounds and $\alpha\alpha'$-bis(dithiobisformamidinium) bromide in hydrobromic acid solutions.

2. Structural commentary

The title compound (Fig. 1) is isostructural to the similar osmium complex (Rudnitskaya *et al.*, 2008, 2019). In the α,α'-(dithiobisformamidinium) cation, the S—S bond is single and has a length of 2.0282 (12) Å, while in the osmium complex the length of this bond is 2.039 (2) Å. The cation adopts the most energetically favorable gauche conformation with a C—S—S—C torsion angle of 97.15 (11)°, which is slightly smaller than the angle in the osmium analogue (102.62°). The intrinsic symmetry of the cations is $C2$, and the thiocarbamide fragments retain a planar structure in both complexes. The intrinsic symmetry of the $[RuBr_6]^{2-}$ ion is $D2h$. The coordination number of ruthenium is 6, and the anion takes the form of a distorted octahedron, $d(Ru-Br)$ = 2.4779 (4)–2.4890 (4) Å for three Br atoms are different, but within standard errors (Table 1). The conformation of the cation is aslo consolidated by intramolecular N—H···S hydrogen bonds (Table 2, Fig. 1). In $[(NH_2)_2CSSC(NH_2)_2]_2$-$[OsBr_6]Br_2 \cdot 3H_2O$, the conformation of the cation is also

Table 1
Selected bond lengths (Å).

Ru1—Br1	2.4779 (4)	Ru1—Br3	2.4866 (3)
Ru1—Br3^i	2.4866 (3)	Ru1—Br2	2.4890 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.80 (4)	2.02 (4)	2.814 (3)	167 (3)
O1—H1C···Br3	0.84 (3)	2.52 (3)	3.293 (3)	154 (4)
O1—H1D···O2	0.84 (3)	2.00 (4)	2.794 (4)	157 (5)
N1—H1B···Br4	0.77 (3)	2.60 (3)	3.327 (3)	157 (3)
N2—H2B···Br1^{ii}	0.81 (3)	2.96 (4)	3.496 (2)	125 (3)
N2—H2A···Br2^{iii}	0.88 (4)	2.79 (4)	3.456 (2)	134 (3)
N2—H2B···Br4	0.81 (3)	2.87 (4)	3.592 (3)	149 (3)
O2—H2···Br4^{iv}	0.95 (5)	2.48 (5)	3.419 (2)	167 (4)

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

stabilized by intramolecular N—H···S hydrogen bonds (Rudnitskaya *et al.*, 2008). The geometric parameters of the title compound are normal and consistent with those of the related compounds described in the *Database survey* (Section 4).

3. Supramolecular features

The $[(NH_2)_2CSSC(NH_2)_2]^{2+}$ cations and $[RuBr_6]^{2-}$ complex anion form a system of hydrogen bonds with the Br$^-$ ions and water molecules (Table 2, Figs. 1 and 2). Two cations are bound in a ring by two Br$^-$ ions, each forming four hydrogen bonds with the NH$_2$ groups of the cations. A similar system of hydrogen bonds is present in the osmium complex.

For two O—H···Br hydrogen bonds [O1—H1C···Br3 and O2—H2···Br4^v, symmetry code: (v) $x - \frac{1}{2}, y + \frac{1}{2}, z$], the average distance of H···Br is 3.356 (3) Å and the average value of the O—H···Br angle is 161 (4)°. For four N—H···Br hydrogen bonds [N1—H1B···Br4, N2—H2B···Br1^{iii},
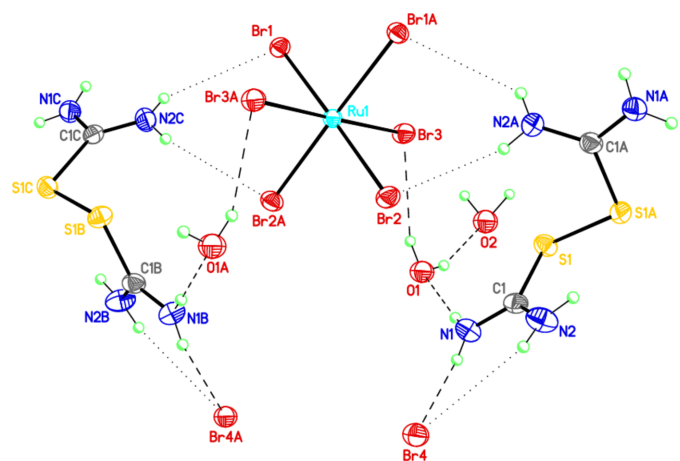
Figure 1
The molecular structure of $[S_2C_2(NH_2)_4]_2[RuBr_6]Br_2 \cdot 3H_2O$, showing the atom labeling and displacement ellipsoids drawn at the 30% probability level. Symmetry codes: (A) $x, y, \frac{3}{2} - z$; (B) $1 - x, y, \frac{3}{2} - z$; (C) $x, 1 - y, 1 - z$.

Table 3
Selected values of bond distances (Å) and angles (°) in various salts and complexes.

Compound	S—S	C—S	C—S—S	C—S—S—C	Reference
Title compound	2.0282 (12)	1.783 (2)	102.90 (9)	−95.15 (11)	This study
XAJVUB	2.024 (2)	1.778 (5)	103.2 (2)	96.3	(Rudnitskaya *et al.*, 2008)
NIPBIA	2.036 (2)	1.789 (5)	102.43 (17)	−96.4 (4)	(Rudnitskaya *et al.*, 2019)
NIPBOG	2.039 (2)	1.796 (5)	102.62 (15)	−97.9 (3)	(Rudnitskaya *et al.*, 2019)
PATCIZ	–	1.739 (10)	–	–	(Rudnitskaya *et al.*, 2017*b*)
PATCOF	–	1.751 (9)	–	–	(Rudnitskaya *et al.*, 2017*b*)

N2—H2A···Br2^{iv}, N2—H2B···Br4, symmetry codes: (iii) $-x + 1$, $-y + 1$, $z - \frac{1}{2}$; (iv) x, $-y + 1$, $-z + 1$], the average H···Br distance is 3.468 (3) Å and the average N—H···Br angle is 141 (3)°. These values show that hydrogen bonds are quite strong.

4. Database survey

A search of the Cambridge Crystallographic Database (updated 20 March 2023; Groom *et al.*, 2016) using the $[\text{RuBr}_6]^{2-}$ complex ion and the $\alpha\alpha'$-bis(dithiobisform-amidinium) cation as the search fragments revealed five closely related compounds, *viz.* bis[α,α'-dithiobis(form-amidinium)] hexabromidoosmium(IV) dibromide trihydrate (CSD refcode XAJVUB; Rudnitskaya *et al.*, 2008), bis-[disulfanediylbis(aminomethaniminium)] bis(chloride) hexa-chloridoosmium(IV) trihydrate (NIPBIA; Rudnitskaya *et al.*, 2019), bis[disulfanediylbis(aminomethaniminium)] bis(bro-mide) hexabromidoosmium(IV) trihydrate (NIPBOG; Rudnitskaya *et al.*, 2019), bis[(diaminomethylene)sulfonium] hexachloridoosmium (PATCIZ; Rudnitskaya *et al.*, 2017*b*) and bis[(diaminomethylene)sulfonium] hexabromidoosmium (PATCOF; Rudnitskaya *et al.*, 2017*b*).
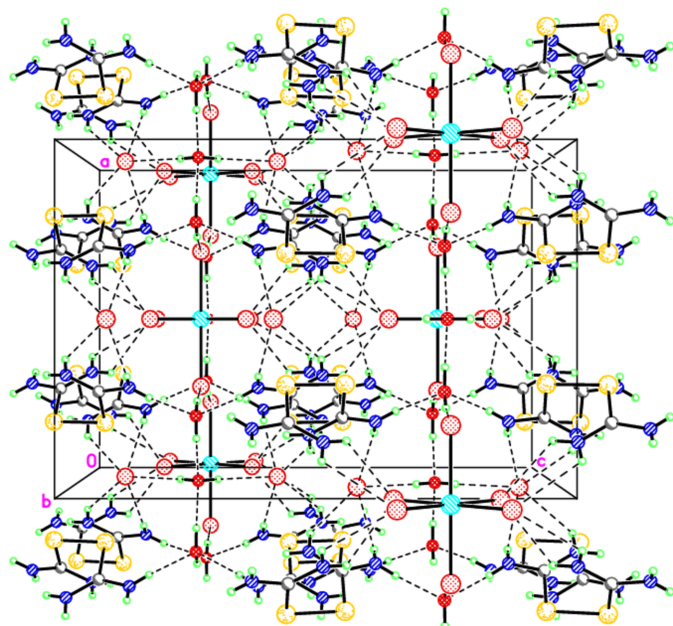
XAJVUB, NIPBIA and NIPBOG crystallize in the ortho-rhombic *Cmcm* space group with $Z = 4$, while PATCIZ and PATCOF crystallize in the triclinic $P\bar{1}$ space group with $Z = 1$. In XAJVUB, the $[\text{OsBr}_6]^{2-}$ anionic complex has an octahedral structure. The Os—Br distances fall in the range 2.483–2.490 Å. The α,α'-dithiobisformamidinium cation is a product of the oxidation of thiocarbamide. The S—S and C—S distances are 2.016 and 1.784 Å, respectively. The water mol-ecules, Br$^-$ ions, and NH$_2$ groups of the cation are linked by hydrogen bonds. In NIPBIA and NIPBOG, the osmium atoms in the $[\text{OsX}_6]^{2-}$ (X = Cl or Br) anions adopt slightly distorted octahedral coordination. The α,α'-dithiobisformamidinium cations are paired into rings by N—H···Cl$^-$ hydrogen bonds. The rings are further connected into a 3D framework by hydrogen bonds involving the water molecules and S···Cl non-covalent interactions. In the crystal structures of PATCIZ and PATCOF, the (NH$_2$)$_2$CSH$^+$ cations and $[\text{OsX}_6]^{2-}$ anions are linked into two-tier layers in the (110) plane by the N—H···X(Cl, Br) and S—H···X(Cl, Br) hydrogen bonds and S···X(Cl, Br) non-covalent attractive contacts. It can be seen from the similar geometric parameter values given in Table 3 that the discussed compounds are comparable with each other.

5. Synthesis and crystallization

Synthesis of [(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$_2$[RuBr$_6$]Br$_2$·3H$_2$O

To 0.10 g of K$_4$[Ru$_2$OCl$_{10}$], 10 mL of concentrated HBr (from Riedel de Haen) were added, and the reaction mixture was heated in a water bath until the K$_4$[Ru$_2$OCl$_{10}$] dissolved completely. Then a solution of 0.13 g of [S$_2$C$_2$(NH$_2$)$_4$]Br$_2$·2H$_2$O (molar ratio Ru:[S$_2$C$_2$(NH$_2$)$_4$]Br$_2$ = 1:1.5) was added, and the resulting solution was evaporated in a water bath to 2–3 ml. Dark, large orthorhombic crystals formed after the solution was cooled. The precipitate was filtered off, and washed with 3 ml of distilled water and 4 ml of ethanol. The mass of the obtained solid was 0.10 g (yield: 67%). Found Ru = 9.6%, for [S$_2$C$_2$(NH$_2$)$_4$]$_2$[RuBr$_6$]Br$_2$·3H$_2$O: calculated Ru = 9.67%. Sulfur and bromine were determined by microanalysis, and ruthenium was determined by reducing the sample to metallic ruthenium in a stream of H$_2$ at 1073 K. Errors between the found and measured values are normal depending on the technique used.

The compound is highly soluble in DMSO, giving blue solutions, while in dilute and concentrated HBr it dissolves over time (red and orange solutions, respectively) and is insoluble in alcohol and acetone.

Figure 2
View of the arrangement and interactions of the [(NH$_2$)$_2$CSSC(NH$_2$)$_2$]$^{2+}$ cations, the RuBr$_6$$^{2-}$ and Br$^-$ anions, and water molecules in the unit cell.

EAS [λ_{max}, nm (ε, mol^{-1} L cm^{-1})]: in HBr (2 mol L^{-1}) – 400 (1800), 460 (1550), 560sh (720); in HBr (9 mol L^{-1}) – 375sh (2850), 390 (2830), 440sh (2050), 455 (2450), 465sh (2400), 520sh (800); in DMSO – 390sh (6700), 480sh (2000), 505sh (2800), 555 (3930), 619 (4060), 686 (3980), 710sh (3000), 755sh (1900).

FTIR (ν, cm^{-1}): 183, 230 ν (Ru—Br); 422 ρ(SCN$_2$), ρ(NH$_2$); 497 δ(CN$_2$); 577 b(SCN$_2$), ν(CS); 815 ν(CS), ν_s(CN), δ(CN$_2$); 1063 ρ(NH$_2$), ν_{as}(CN); 1119, 1385 ν_s(CN), ν(CS), ρ(NH$_2$); 1621, 1627, 1645 δ(NH$_2$), δ(OH$_2$), ν_{as}(CN); 3050 ν(NH), 3260, 3400 ν_{as}(NH), ν(OH).

The reaction with K$_4$[Ru$_2$OCl$_{10}$] was carried out similarly at a ratio of Ru:[S$_2$C$_2$(NH$_2$)$_4$]$^{2+}$ = 1:2, and reactions with ruthenium trichlorides were carried out using ratios of reactants of 1:1.5 and 1:2.

As a result of all experiments, [S$_2$C$_2$(NH$_2$)$_4$]$_2$[RuBr$_6$]Br$_2$·3H$_2$O precipitates formed, but when the ratio of the initial components was 1:2, the precipitates contained an admixture of [S$_2$C$_2$(NH$_2$)$_4$]Br$_2$·2H$_2$O.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All hydrogen atoms were derived from the Fourier synthesis map and refined isotropically with dependent isotropic thermal parameters with U_{iso}(H) = 1.2U_{eq}(N) and U_{iso}(H) = 1.5U_{eq}(O).

Table 4
Experimental details.

Crystal data	
Chemical formula	(C$_2$H$_8$N$_4$S$_2$)$_2$[RuBr$_6$]Br$_2$·3H$_2$O
M_r	1098.88
Crystal system, space group	Orthorhombic, *Cmcm*
Temperature (K)	150
a, b, c (Å)	11.6462 (3), 13.9943 (4), 16.9225 (5)
V (Å^3)	2758.04 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	12.49
Crystal size (mm)	0.30 × 0.20 × 0.02
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.043, 0.100
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22642, 2269, 2057
R_{int}	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.057, 1.07
No. of reflections	2269
No. of parameters	93
No. of restraints	1
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.06, −0.59

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2019/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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supporting information

Synthesis, molecular and crystal structure of [(NH₂)₂CSSC(NH₂)₂]₂[RuBr₆]Br₂·3H₂O

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Computing details

Bis[dithiobis(formamidinium)] hexabromidoruthenium dibromide trihydrate

Crystal data

$(C_2H_8N_4S_2)_2[RuBr_6]Br_2\cdot3H_2O$	$D_x = 2.646$ Mg m^{-3}
$M_r = 1098.88$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Cmcm*	Cell parameters from 1291 reflections
$a = 11.6462$ (3) Å	$\theta = 2.3–26.6°$
$b = 13.9943$ (4) Å	$\mu = 12.49$ mm^{-1}
$c = 16.9225$ (5) Å	$T = 150$ K
$V = 2758.04$ (13) Å^3	Plate, black
$Z = 4$	$0.30 \times 0.20 \times 0.02$ mm
$F(000) = 2056$	

Data collection

Bruker D8 Venture diffractometer	2269 independent reflections
Radiation source: microsource	2057 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.043$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 30.5°$, $\theta_{min} = 2.3°$
$T_{min} = 0.043$, $T_{max} = 0.100$	$h = -16\rightarrow16$
22642 measured reflections	$k = -19\rightarrow20$
	$l = -24\rightarrow24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.023$	Only H-atom coordinates refined
$wR(F^2) = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 6.898P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	
2269 reflections	$(\Delta/\sigma)_{max} = 0.001$
93 parameters	$\Delta\rho_{max} = 1.06$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.59$ e Å^{-3}
Primary atom site location: difference Fourier map	

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*	$U_{iso}*/U_{eq}$
Ru1	0.500000	0.65423 (2)	0.750000	0.01754 (8)
Br1	0.500000	0.77930 (2)	0.85365 (2)	0.02178 (8)
Br2	0.500000	0.52583 (2)	0.64822 (2)	0.02559 (8)
Br3	0.28649 (3)	0.65551 (2)	0.750000	0.02565 (9)
Br4	0.500000	0.17169 (2)	0.58416 (2)	0.02717 (9)
S1	0.18284 (5)	0.47494 (4)	0.55623 (4)	0.02521 (13)
N1	0.2957 (2)	0.33273 (17)	0.61812 (15)	0.0280 (5)
H1A	0.264 (3)	0.353 (2)	0.657 (2)	0.034*
H1B	0.330 (3)	0.285 (2)	0.616 (2)	0.034*
N2	0.3321 (2)	0.35163 (17)	0.48633 (16)	0.0329 (5)
H2A	0.331 (3)	0.386 (3)	0.443 (2)	0.039*
H2B	0.380 (3)	0.310 (2)	0.489 (2)	0.039*
C1	0.2816 (2)	0.37771 (17)	0.55165 (16)	0.0241 (5)
O1	0.2061 (2)	0.4299 (2)	0.750000	0.0305 (6)
H1C	0.249 (4)	0.478 (3)	0.750000	0.046*
H1D	0.136 (3)	0.445 (4)	0.750000	0.046*
O2	0.000000	0.5321 (3)	0.750000	0.0360 (9)
H2	0.000000	0.579 (4)	0.709 (3)	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.01735 (16)	0.01668 (16)	0.01860 (17)	0.000	0.000	0.000
Br1	0.02324 (15)	0.02066 (15)	0.02144 (16)	0.000	0.000	−0.00283 (11)
Br2	0.03078 (18)	0.02150 (16)	0.02447 (17)	0.000	0.000	−0.00468 (12)
Br3	0.01777 (15)	0.02213 (16)	0.0371 (2)	−0.00096 (11)	0.000	0.000
Br4	0.02496 (16)	0.02304 (16)	0.0335 (2)	0.000	0.000	0.00104 (13)
S1	0.0280 (3)	0.0238 (3)	0.0238 (3)	0.0043 (2)	0.0033 (2)	0.0016 (2)
N1	0.0287 (11)	0.0256 (11)	0.0298 (12)	0.0040 (8)	0.0033 (9)	0.0043 (9)
N2	0.0370 (13)	0.0272 (11)	0.0345 (13)	0.0063 (10)	0.0128 (11)	0.0034 (10)
C1	0.0228 (11)	0.0199 (10)	0.0295 (13)	−0.0019 (9)	0.0023 (9)	0.0015 (9)
O1	0.0329 (14)	0.0254 (13)	0.0333 (15)	0.0003 (11)	0.000	0.000
O2	0.042 (2)	0.032 (2)	0.035 (2)	0.000	0.000	0.000

Geometric parameters (Å, º)

Ru1—Br1	2.4779 (4)	N1—H1A	0.80 (4)
Ru1—Br1[i]	2.4779 (4)	N1—H1B	0.77 (3)
Ru1—Br3[ii]	2.4866 (3)	N2—C1	1.305 (3)

Ru1—Br3	2.4866 (3)	N2—H2A	0.88 (4)
Ru1—Br2ⁱ	2.4890 (4)	N2—H2B	0.81 (3)
Ru1—Br2	2.4890 (4)	O1—H1C	0.84 (3)
S1—C1	1.783 (2)	O1—H1D	0.84 (3)
S1—S1ⁱⁱⁱⁱ	2.0282 (12)	O2—H2	0.95 (5)
N1—C1	1.299 (3)		
Br1—Ru1—Br1ⁱ	90.122 (19)	Br3—Ru1—Br2	90.298 (8)
Br1—Ru1—Br3ⁱⁱ	89.708 (8)	Br2ⁱ—Ru1—Br2	87.58 (2)
Br1ⁱ—Ru1—Br3ⁱⁱ	89.708 (8)	C1—S1—S1ⁱⁱⁱⁱ	102.90 (9)
Br1—Ru1—Br3	89.708 (8)	C1—N1—H1A	119 (2)
Br1ⁱ—Ru1—Br3	89.708 (8)	C1—N1—H1B	117 (3)
Br3ⁱⁱ—Ru1—Br3	179.17 (2)	H1A—N1—H1B	124 (4)
Br1—Ru1—Br2ⁱ	91.151 (12)	C1—N2—H2A	123 (2)
Br1ⁱ—Ru1—Br2ⁱ	178.727 (16)	C1—N2—H2B	117 (3)
Br3ⁱⁱ—Ru1—Br2ⁱ	90.298 (8)	H2A—N2—H2B	117 (3)
Br3—Ru1—Br2ⁱ	90.298 (8)	N1—C1—N2	122.7 (2)
Br1—Ru1—Br2	178.729 (16)	N1—C1—S1	114.4 (2)
Br1ⁱ—Ru1—Br2	91.150 (12)	N2—C1—S1	122.8 (2)
Br3ⁱⁱ—Ru1—Br2	90.298 (8)	H1C—O1—H1D	112 (5)
S1ⁱⁱⁱⁱ—S1—C1—N1	−179.53 (18)	S1ⁱⁱⁱⁱ—S1—C1—N2	−2.0 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.80 (4)	2.02 (4)	2.814 (3)	167 (3)
O1—H1*C*···Br3	0.84 (3)	2.52 (3)	3.293 (3)	154 (4)
O1—H1*D*···O2	0.84 (3)	2.00 (4)	2.794 (4)	157 (5)
N1—H1*B*···Br4	0.77 (3)	2.60 (4)	3.327 (2)	157 (3)
N2—H2*B*···Br1^{iv}	0.81 (3)	2.96 (4)	3.496 (2)	125 (3)
N2—H2*A*···Br2ⁱⁱⁱ	0.88 (4)	2.79 (4)	3.456 (2)	134 (3)
N2—H2*B*···Br4	0.81 (3)	2.87 (4)	3.592 (3)	149 (3)
O2—H2···Br4^v	0.95 (5)	2.48 (5)	3.419 (2)	167 (4)

Symmetry codes: (iii) *x*, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+1, *z*−1/2; (v) *x*−1/2, *y*+1/2, *z*.