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The Crystal and Molecular Structure of Sulphatobis(thiocarbonohydrazide-*N,S*)-copper(II) Tetrahydrate

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Crystals of the title compound are monoclinic with $a = 13\cdot430$ (5), $b = 8\cdot340$ (3), $c = 17\cdot070$ (9) Å, $\beta = 122\cdot8$ (1)°, $Z = 4$, space group $P2_1/c$. The structure was solved from diffractometric data by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to $R = 0\cdot044$ for 2185 observed reflexions. The structure consists of $Cu[SC(NHNH_2)_2]_2SO_4$ complexes and water molecules, linked by hydrogen bonds. The coordination polyhedron around copper is a square pyramid whose base is formed by two sulphur (Cu–S $= 2\cdot260$, $2\cdot263$ Å) and two nitrogen (Cu–N $= 2\cdot011$, $2\cdot015$ Å) atoms of two chelating thiocarbonohydrazide molecules. The apex of the pyramid is occupied by an oxygen (Cu–O $= 2\cdot794$ Å) atom from the sulphate group. A long Cu$\cdots$S contact ($3\cdot476$ Å), in the direction of the d_z^2 orbitals of the metal, completes the distorted octahedral coordination, joining the complexes to form dimers.

Introduction

Thiocarbonohydrazide (tcaz), $SC(NH–NH_2)_2$, can assume a *cis,trans*-conformation, *i.e.* with the $-NH-NH_2$ groups rotated differently with respect to the S–C bond, or a *cis,cis*-conformation, *i.e.* with both $-NH-NH_2$ groups bent towards the S–C bond. The *cis,trans*-conformation (I) has been found when tcaz is neutral (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969) or monoprotonated (Braibanti, Tiripicchio & Tiripicchio Camellini, 1972). The *cis,cis*-conformation (II) is assumed when tcaz is diprotonated (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Bigoli, Braibanti, Manotti Lanfredi & Tiripicchio, 1972).

(I)   (II)
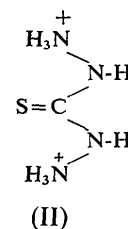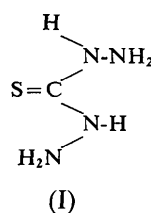
Conformation (I) is also present in metal complexes where penta-atomic chelate rings with S and N as donor atoms are formed (Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1971). Structures of this type have been assumed to interpret the i.r. spectra (Burns, 1968) and the equilibria in solution (Braibanti, Dallavalle & Leporati, 1969) for several complexes. This behaviour is confirmed by the crystal-structure analysis of the title compound which is described in the present paper.

Experimental

Preparation

Violet crystals of the compound were obtained by adding tcaz to solutions of copper sulphate (tcaz: $CuSO_4$ in stoichiometric ratio).

Crystal data

$C_2H_{20}CuN_8O_8S_3$, F.W. 443·99. The unit-cell parameters were determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer, $\bar{\lambda}(Cu\,K\alpha) = 1·5418$ Å: $a = 13·430$ (5), $b = 8·340$ (3), $c = 17·070$ (9) Å; $\beta = 122·8$ (1)°; $V = 1607·4$ Å^3, $Z = 4$; $D_x = 1·834$, $D_m = 1·845$ g cm^{-3}; $F(000) = 916$; $\mu(Cu\,K\alpha) = 59·37$ cm^{-1}; space group: $P2_1/c$ from systematic absences.

Intensity data

Intensities were collected on a Siemens AED single-crystal on-line diffractometer with nickel-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. The crystal was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflexions with $2\theta \le 140°$ were measured. Of 3223 independent reflexions 2185 with $I \ge 2\sigma(I)$ were used in the structure determination. Corrections for Lorentz and polarization effects were

Table 1. *Final fractional atomic coordinates*
($\times 10^4$) with e.s.d.'s

	x	y	z
Cu	1298 (1)	415 (1)	1463 (1)
S(11)	707 (1)	2173 (2)	280 (1)
S(12)	3004 (1)	−255 (2)	1580 (1)
S(3)	2009 (1)	2377 (1)	3627 (1)
O(1)	1757 (3)	781 (4)	3862 (3)
O(2)	871 (3)	3203 (4)	3012 (3)
O(3)	2591 (4)	2167 (5)	3116 (3)
O(4)	2734 (4)	3313 (5)	4480 (3)
O_w(1)	643 (3)	5533 (4)	1761 (3)
O_w(2)	3725 (4)	4031 (5)	2426 (3)
O_w(3)	3067 (4)	6599 (5)	4436 (3)
O_w(4)	5066 (5)	1379 (8)	4396 (5)
N(11)	−952 (4)	2067 (5)	689 (3)
N(12)	2842 (4)	−1917 (5)	2846 (3)
N(21)	−188 (4)	990 (5)	1416 (3)
N(22)	1699 (4)	−1263 (5)	2441 (3)
N(31)	−1332 (4)	3717 (5)	−514 (3)
N(32)	4598 (4)	−2086 (6)	2915 (3)
N(41)	−2426 (4)	4219 (5)	−677 (3)
N(42)	4977 (4)	−3100 (7)	3733 (3)
C(11)	−611 (4)	2683 (6)	160 (3)
C(12)	3520 (4)	−1499 (6)	2532 (4)
H(11)	−1697 (39)	2193 (57)	563 (31)
H(12)	3197 (49)	−2577 (72)	3384 (39)
H(21)	−712 (45)	136 (66)	1376 (36)
H(22)	1206 (42)	−2012 (60)	2257 (33)
H(31)	51 (43)	1572 (62)	1947 (34)
H(32)	1697 (42)	−797 (61)	2905 (33)
H(41)	−1047 (42)	4076 (60)	−829 (33)
H(42)	5212 (48)	−1829 (70)	2812 (37)
H(51)	−2924 (51)	3371 (73)	−808 (40)
H(52)	5791 (55)	−2686 (82)	4153 (44)
H(61)	−2210 (45)	4825 (67)	−151 (36)
H(62)	4930 (58)	−4038 (84)	3514 (46)
H_w(11)	−125 (49)	5626 (71)	1519 (39)
H_w(21)	870 (49)	4827 (72)	2222 (38)
H_w(12)	3251 (58)	3636 (83)	2638 (46)
H_w(22)	3121 (59)	4703 (90)	1951 (46)
H_w(13)	3833 (55)	7058 (81)	4897 (43)
H_w(23)	3275 (70)	5634 (105)	4392 (56)
H_w(14)	4996 (79)	1734 (108)	4904 (62)
H_w(24)	4197 (69)	1445 (101)	3990 (55)

Table 2. *Thermal parameters with e.s.d.'s* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2·130 (22)	1·306 (20)	2·321 (25)	0·288 (20)	1·501 (20)	0·408 (21)
S(11)	2·525 (53)	1·743 (46)	2·885 (58)	0·328 (41)	1·971 (47)	0·681 (44)
S(12)	2·438 (51)	2·030 (49)	2·866 (58)	0·136 (43)	1·878 (46)	0·341 (46)
S(3)	2·062 (48)	1·493 (44)	1·955 (50)	0·043 (38)	1·062 (41)	0·117 (39)
O(1)	3·567 (175)	1·525 (142)	2·710 (166)	0·317 (123)	2·133 (146)	0·607 (120)
O(2)	2·904 (164)	1·835 (146)	2·610 (165)	0·601 (127)	1·357 (139)	0·326 (125)
O(3)	4·392 (208)	3·134 (186)	5·246 (234)	−0·041 (164)	3·883 (196)	0·283 (175)
O(4)	4·640 (234)	3·030 (195)	2·930 (192)	−1·208 (175)	0·372 (175)	−0·367 (159)
O_w(1)	3·012 (160)	2·286 (150)	2·618 (160)	0·039 (134)	1·907 (137)	0·543 (134)
O_w(2)	2·909 (174)	3·147 (182)	3·813 (201)	0·093 (146)	1·880 (159)	0·926 (158)
O_w(3)	2·963 (170)	2·795 (171)	3·658 (196)	0·435 (144)	1·924 (154)	0·607 (151)
O_w(4)	4·418 (282)	6·979 (373)	7·962 (387)	−0·319 (264)	0·739 (268)	−0·522 (312)
N(11)	1·920 (159)	2·106 (170)	1·614 (165)	0·212 (137)	1·003 (136)	0·560 (142)
N(12)	1·920 (166)	2·406 (184)	2·494 (191)	0·595 (144)	1·325 (151)	0·569 (155)
N(21)	2·132 (169)	1·481 (152)	2·075 (177)	0·076 (132)	1·212 (147)	0·373 (135)
N(22)	1·974 (165)	1·590 (160)	2·096 (183)	0·048 (132)	1·105 (145)	0·254 (137)
N(31)	2·269 (176)	1·402 (160)	2·606 (198)	0·211 (136)	1·256 (155)	0·470 (143)
N(32)	2·024 (176)	2·969 (208)	2·904 (206)	0·564 (156)	1·218 (162)	0·224 (172)
N(41)	2·450 (182)	2·064 (184)	2·395 (198)	0·179 (145)	1·217 (158)	0 152 (147)
N(42)	3·018 (216)	3·912 (244)	2·665 (212)	1·306 (188)	1·385 (180)	0·379 (187)
C(11)	2·102 (192)	1·402 (170)	1·339 (187)	−0·203 (147)	1·019 (158)	−0·157 (145)
C(12)	2·331 (205)	1·335 (174)	2·315 (218)	−0·248 (156)	1·393 (178)	−0·699 (159)

Table 2 (cont.)

	B
H(11)	1·32 (0·95)
H(12)	3·47 (1·34)
H(21)	2·62 (1·17)
H(22)	1·86 (1·05)
H(31)	2·12 (1·09)
H(32)	1·94 (1·06)
H(41)	1·83 (1·04)
H(42)	3·09 (1·27)
H(51)	3·70 (1·38)
H(52)	4·72 (1·57)
H(61)	2·74 (1·18)
H(62)	5·28 (1·70)
$H_w(11)$	3·47 (1·32)
$H_w(21)$	3·47 (1·33)
$H_w(12)$	5·22 (1·68)
$H_w(22)$	5·70 (1·76)
$H_w(13)$	4·50 (1·54)
$H_w(23)$	7·96 (2·27)
$H_w(14)$	8·52 (2·34)
$H_w(24)$	7·68 (2·23)

made, but not for absorption. The absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's (1942) method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods. Refinement was carried out by block-diagonal least-squares calculations, first with isotropic, then with anisotropic thermal parameters. The hydrogen atoms were located from a difference synthesis. Further least-squares cycles were computed including the hydrogen atoms with isotropic thermal parameters. Unit weights were assumed for every reflexion in all stages of the refinement. The final R was 0·044.
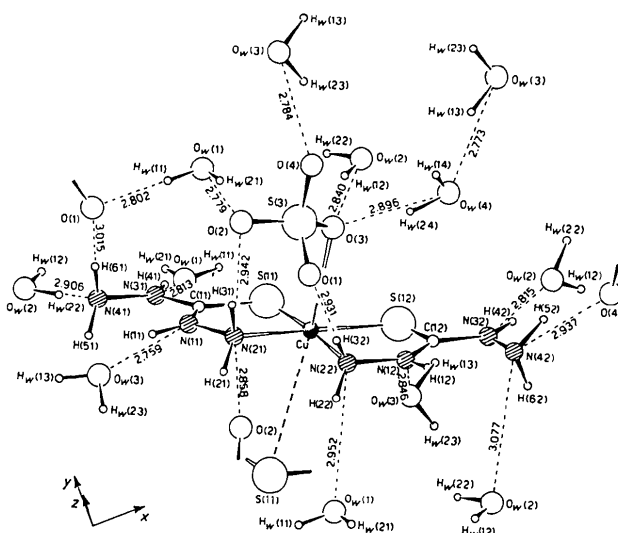

Fig. 1. Clinographic projection of the structure.

Atomic coordinates and thermal parameters are given in Tables 1 and 2.*

Table 3. *Bond distances and angles*

(a) In the coordination polyhedron

Cu–S(11)	2·263 (3)	S(11)–Cu–N(21)	87·1 (0·1)°
Cu–S(12)	2·260 (2)	S(11)–Cu–S(12)	95·0 (0·1)
Cu–N(21)	2·011 (6)	S(12)–Cu–N(22)	87·2 (0·2)
Cu–N(22)	2·015 (5)	N(22)–Cu–N(21)	90·7 (0·2)
Cu–O(3)	2·794 (5)	N(22)–Cu–O(3)	77·6 (0·2)
		N(21)–Cu–O(3)	88·6 (0·2)
		S(11)–Cu–O(3)	106·7 (0·1)
		S(12)–Cu–O(3)	89·7 (0·1)

(b) In the sulphate anion

S(3)–O(1)	1·481 (4)	O(1)–S(3)–O(2)	108·2 (0·3)
S(3)–O(2)	1·475 (4)	O(1)–S(3)–O(3)	109·2 (0·2)
S(3)–O(3)	1·463 (7)	O(1)–S(3)–O(4)	109·7 (0·3)
S(3)–O(4)	1·463 (5)	O(2)–S(3)–O(3)	108·3 (0·3)
		O(2)–S(3)–O(4)	109·5 (0·3)
		O(3)–S(3)–O(4)	112·0 (0·3)

(c) In the thiocarbonohydrazide molecules

S(11)–C(11)	1·721 (6)	S(11)–C(11)–N(11)	122·6 (0·4)
C(11)–N(11)	1·318 (9)	S(11)–C(11)–N(31)	118·6 (0·4)
N(11)–N(21)	1·421 (6)	N(31)–C(11)–N(11)	118·8 (0·6)
C(11)–N(31)	1·341 (6)	C(11)–N(11)–N(21)	119·3 (0·5)
N(31)–N(41)	1·403 (8)	C(11)–N(31)–N(41)	123·6 (0·5)
N(11)–H(11)	0·91 (6)	C(11)–N(11)–H(11)	122·7 (3·0)
N(21)–H(21)	0·98 (6)	H(11)–N(11)–N(21)	117·5 (3·0)
N(21)–H(31)	0·92 (6)	N(11)–N(21)–H(21)	104·3 (3·3)
N(31)–H(41)	0·87 (7)	H(21)–N(21)–H(31)	107·9 (5·0)
N(41)–H(51)	0·91 (6)	N(11)–N(21)–H(31)	103·2 (3·3)
N(41)–H(61)	0·93 (6)	C(11)–N(31)–H(41)	113·5 (3·7)
		H(41)–N(31)–N(41)	122·8 (3·7)
		H(31)–N(41)–H(51)	111·5 (4·5)
		H(51)–N(41)–H(61)	117·5 (5·7)
		N(31)–N(41)–H(61)	103·0 (4·1)
S(12)–C(12)	1·726 (6) Å	S(12)–C(12)–N(12)	121·6 (0·5)
C(12)–N(12)	1·329 (10)	S(12)–C(12)–N(32)	119·9 (0·5)
N(12)–N(22)	1·408 (7)	N(12)–C(12)–N(32)	118·5 (0·5)
C(12)–N(32)	1·314 (7)	C(12)–N(23)–N(42)	117·5 (0·5)
N(32)–N(42)	1·421 (7)	C(12)–N(12)–N(22)	120·2 (0·4)
N(12)–H(12)	0·95 (6)	C(12)–N(12)–H(12)	116·6 (4·6)
N(22)–H(22)	0·84 (5)	H(12)–N(12)–N(22)	122·9 (4·6)
N(22)–H(32)	0·88 (6)	N(12)–N(22)–H(22)	109·0 (3·9)
N(32)–H(42)	1·00 (8)	H(22)–N(22)–H(32)	106·2 (5·4)
N(42)–H(52)	0·99 (6)	N(12)–N(22)–H(32)	105·2 (3·7)
N(42)–H(62)	0·85 (7)	C(12)–N(32)–H(42)	126·9 (3·3)
		H(42)–N(32)–N(42)	115·5 (3·3)
		N(32)–N(42)–H(52)	99·5 (3·9)
		H(52)–N(42)–H(62)	115·3 (7·0)
		N(32)–N(42)–H(62)	103·3 (4·6)

(d) In the water molecules

$O_w(1)–H_w(11)$	0·88 (6)	$H_w(11)–O_w(1)–H_w(21)$	103·0 (6·1)
$O_w(1)–H_w(21)$	0·89 (6)		
$O_w(2)–H_w(12)$	0·95 (9)	$H_w(12)–O_w(2)–H_w(22)$	95·2 (6·8)
$O_w(2)–H_w(22)$	0·96 (6)		
$O_w(3)–H_w(13)$	0·97 (6)	$H_w(13)–O_w(3)–H_w(23)$	100·7 (7·6)
$O_w(3)–H_w(23)$	0·87 (9)		
$O_w(4)–H_w(14)$	0·97 (12)	$H_w(14)–O_w(4)–H_w(24)$	87·7 (8·3)
$O_w(4)–H_w(24)$	0·98 (8)		

Scattering factors of Cromer & Mann (1968) were used for Cu,S,N,C,O and of Stewart, Davidson & Simpson (1965) for H.

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) with the programs written by Immirzi (1967).

Discussion

A clinographic projection of the structure is shown in Fig. 1. Bond distances and angles are given in Table 3.

The structure consists of sulphatobis(tcaz)copper(II) complexes with two crystallographically distinct tcaz ligands, and of four molecules of water of crystallization which link the complexes by hydrogen bonds.

Copper is in a five-coordinate square-pyramidal configuration (Fig. 2), the base of which is formed by sulphur and nitrogen atoms, S(11), S(12), N(21) and N(22), in cis-configuration, from two chelating tcaz molecules. The conformation of the two tcaz molecules is the expected cis,trans. The nitrogen and sulphur atoms forming the base of the pyramid show a very slight tetrahedral distortion and the copper atom is slightly displaced towards the top of the pyramid (Table 4). The apex of the pyramid [Cu–O(3) = 2·794 Å] is occupied by an oxygen atom from the SO$_4^{2-}$ group, which behaves as a monodentate ligand, being involved in a rather long Cu–O interaction. A stronger Cu–O (2·340 Å) interaction has been found by Chiesi Villa, Gaetani Manfredotti & Guastini (1972) in sulphatobis(thiosemicarbazide)copper(II) which has a similar structure.

The sixth octahedral coordination site of copper is occupied by S(11) from an adjacent complex at a distance (Cu···S = 3·476 Å) much greater than those usually considered as bond interactions. The angles formed by the Cu···S(11) direction with the other bonds in the coordination polyhedron are: S(11)–

Cu–S(11)* = 84·5, S(12)–Cu–S(11)* = 101·6, N(21)–Cu–S(11)* = 79·8, N(22)–Cu–S(11)* = 90·8, O(3)–Cu–S(11)* = 163·5° (the asterisk indicates the $-x, -y, -z$ transformation). Because of this weak interaction between complexes, loosely bound dimers are formed.

The two chelate rings are practically equal and the penta-atomic coordination rings show the same distortion: the tcaz parts of the rings are planar, whereas the copper atom is appreciably displaced from these planes (Table 4).

Each tcaz molecule as a whole (except for the hydrogen atoms) is approximately in a plane (maximum displacement 0·02 and 0·03 Å in the two molecules respectively).

The geometry of the sulphate anion is normal. Two intramolecular hydrogen bonds join O(1) and O(2) to N(22) and N(21) of the chelating tcaz molecules.

A dense network of intermolecular hydrogen bonds (sulphate...water, tcaz...water and sulphate...tcaz) determines the packing (Table 5).
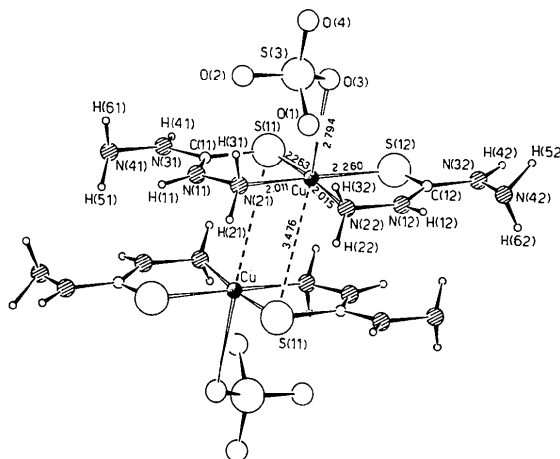

Fig. 2. Coordination around the copper atom.

Table 4. Equations of least-squares planes and deviations of the atoms from the plane

Equations of planes are in the form: $AX + BY + CZ = D$ where X, Y, Z are the coordinates in Å referred to orthogonal axes and obtained from fractional ones by applying the matrix: $a\ 0\ c\cos\beta/0\ b\ 0/0\ 0\ c\sin\beta$.

Plane		A	B	C	D	Deviations (Å) of the atoms from the plane					
I	S(11), S(12), N(21), N(22)	−0·1255	−0·7277	−0·6743	−1·6866	S(11)	0·01	S(12)	−0·01	N(21)	−0·09
						N(22)	0·09	Cu	−0·03	O(3)	−2·72
II	S(11), C(11), N(11), N(21)	−0·1221	−0·7637	−0·6340	−1·7240	S(11)	0·00	C(11)	−0·01	N(11)	0·01
						N(21)	−0·00	Cu	0·08	N(31)	−0·02
						N(41)	−0·03				
III	S(12), C(12), N(12), N(22)	−0·0377	−0·7859	−0·6172	−1·3306	S(12)	0·00	C(12)	−0·02	N(12)	0·02
						N(22)	−0·00	Cu	−0·25	N(32)	−0·05
						N(42)	−0·07				
IV	S(11), C(11), N(11), N(31)	−0·1209	−0·7553	−0·6442	−1·7116	S(11)	0·00	C(11)	−0·01	N(11)	0·00
						N(31)	0·00	N(21)	−0·03	N(41)	−0·00
V	S(12), C(12), N(12), N(32)	−0·0084	−0·7927	−0·6096	−1·2354	S(12)	0·00	C(12)	−0·01	N(12)	0·00
						N(32)	0·00	N(22)	−0·06	N(42)	−0·01
VI	S(11), C(11), N(11), N(21), N(31), N(41)	−0·1249	−0·7595	−0·6386	−1·7193	S(11)	0·00	C(11)	−0·01	N(11)	0·02
						N(21)	−0·01	N(31)	0·00	N(41)	−0·00
VII	S(12), C(12), N(12), N(22), N(32), N(42)	−0·0250	−0·7939	−0·6075	−1·2733	S(12)	0·00	C(12)	−0·00	N(12)	0·03
						N(22)	−0·02	N(32)	−0·00	N(42)	−0·01

Table 5. Hydrogen bonds

Asymmetric units

i	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$		v	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
ii	$-x, 1-y, -z$		vi	$1-x, -y, 1-z$
iii	$-x, \frac{1}{2}+y, \frac{1}{2}-z$		vii	$1-x, 1-y, 1-z$
iv	$x, -1+y, z$			

$N(11)-H(11)\cdots O_w(3^i)$	2·759 (8) Å	$N(11)-H(11)\cdots O_w(3^i)$	155·4 (4·3)°
$H(11)\cdots O_w(3^i)$	1·91 (6)	$H(11)-N(11)\cdots O_w(3^i)$	16·7 (3·0)
$N(21)-H(21)\cdots O(2^i)$	2·858 (7)	$N(21)-H(21)\cdots O(2^i)$	146·1 (4·7)
$H(21)\cdots O(2^i)$	1·99 (6)	$H(21)-N(21)\cdots O(2^i)$	22·9 (3·2)
$N(21)-H(31)\cdots O(2)$	2·942 (6)	$N(21)-H(31)\cdots O(2)$	163·4 (5·5)
$H(31)\cdots O(2)$	2·05 (5)	$H(31)-N(21)\cdots O(2)$	11·5 (3·8)
$N(31)-H(41)\cdots O_w(1^{ii})$	2·813 (9)	$N(31)-H(41)\cdots O_w(1^{ii})$	165·7 (4·7)
$H(41)\cdots O_w(1^{ii})$	1·97 (7)	$H(41)-N(31)\cdots O_w(1^{ii})$	9·9 (3·3)
$N(41)-H(61)\cdots O(1^{iii})$	3·015 (7)	$N(41)-H(61)\cdots O(1^{iii})$	169·1 (5·1)
$H(61)\cdots O(1^{iii})$	2·10 (6)	$H(61)-N(41)\cdots O(1^{iii})$	7·6 (3·5)
$N(12)-H(12)\cdots O_w(3^{iv})$	2·846 (8)	$N(12)-H(12)\cdots O_w(3^{iv})$	145·0 (6·3)
$H(12)\cdots O_w(3^{iv})$	2·02 (8)	$H(12)-N(12)\cdots O_w(3^{iv})$	24·0 (4·5)
$N(22)-H(22)\cdots O_w(1^{iv})$	2·952 (5)	$N(22)-H(22)\cdots O_w(1^{iv})$	151·6 (5·7)
$H(22)\cdots O_w(1^{iv})$	2·19 (5)	$H(22)-N(22)\cdots O_w(1^{iv})$	20·6 (4·1)
$N(22)-H(32)\cdots O(1)$	2·931 (7)	$N(22)-H(32)\cdots O(1)$	166·3 (4·9)
$H(32)\cdots O(1)$	2·07 (6)	$H(32)-N(22)\cdots O(1)$	9·6 (3·4)
$N(32)-H(42)\cdots O_w(2^v)$	2·815 (9)	$N(32)-H(42)\cdots O_w(2^v)$	169·3 (5·3)
$H(42)\cdots O_w(2^v)$	1·83 (7)	$H(42)-N(32)\cdots O_w(2^v)$	6·9 (3·4)
$N(42)-H(52)\cdots O(4^{vi})$	2·937 (7)	$N(42)-H(52)\cdots O(4^{vi})$	135·0 (5·5)
$H(52)\cdots O(4^{vi})$	2·15 (5)	$H(52)-N(42)\cdots O(4^{vi})$	31·2 (3·9)
$N(42)-H(62)\cdots O_w(2^{iv})$	3·077 (7)	$N(42)-H(62)\cdots O_w(2^{iv})$	146·9 (7·1)
$H(62)\cdots O_w(2^{iv})$	2·33 (6)	$H(62)-N(42)\cdots O_w(2^{iv})$	24·3 (5·3)
$O_w(1)-H_w(11)\cdots O(1^{iii})$	2·802 (6)	$O_w(1)-H_w(11)\cdots O(1^{iii})$	173·2 (5·6)
$H_w(11)\cdots O(1^{iii})$	1·92 (7)	$H_w(11)-O_w(1)\cdots O(1^{iii})$	4·7 (3·9)
$O_w(1)-H_w(21)\cdots O(2)$	2·779 (7)	$O_w(1)-H_w(21)\cdots O(2)$	163·3 (6·5)
$H_w(21)\cdots O(2)$	1·91 (7)	$H_w(21)-O_w(1)\cdots O(2)$	11·4 (4·5)
$O_w(2)-H_w(12)\cdots O(3)$	2·840 (9)	$O_w(2)-H_w(12)\cdots O(3)$	160·1 (6·7)
$H_w(12)\cdots O(3)$	1·93 (9)	$H_w(12)-O_w(2)\cdots O(3)$	13·4 (4·4)
$O_w(2)-H_w(22)\cdots N(41^{ii})$	2·906 (7)	$O_w(2)-H_w(22)\cdots N(41^{ii})$	147·6 (7·3)
$H_w(22)\cdots N(41^{ii})$	2·05 (7)	$H_w(22)-O_w(2)\cdots N(41^{ii})$	22·2 (5·0)
$O_w(3)-H_w(13)\cdots O_w(4^{vii})$	2·773 (8)	$O_w(3)-H_w(13)\cdots O_w(4^{vii})$	158·1 (6·2)
$H_w(13)\cdots O_w(4^{vii})$	1·85 (6)	$H_w(13)-O_w(3)\cdots O_w(4^{vii})$	14·4 (4·1)
$O_w(3)-H_w(23)\cdots O(4)$	2·784 (6)	$O_w(3)-H_w(23)\cdots O(4)$	135·0 (9·3)
$H_w(23)\cdots O(4)$	2·10 (9)	$H_w(23)-O_w(3)\cdots O(4)$	32·2 (6·9)
$O_w(4)-H_w(24)\cdots O(3)$	2·896 (8)	$O_w(4)-H_w(24)\cdots O(3)$	163·8 (7·6)
$H_w(24)\cdots O(3)$	1·94 (7)	$H_w(24)-O_w(4)\cdots O(3)$	10·8 (5·0)

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