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Di-μ-thiosemicarbazide-κ^4S:S-bis[bis(thiosemicarbazide-κS)copper(I)] diiodide

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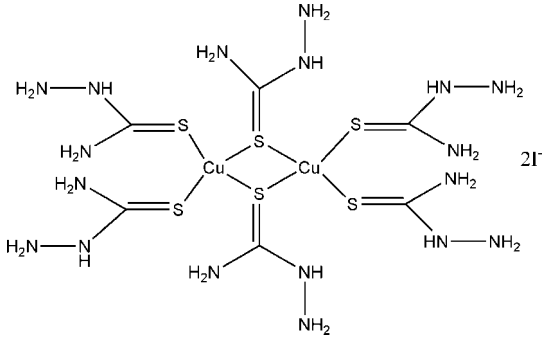
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(N–C) = 0.006 Å; R factor = 0.038; wR factor = 0.106; data-to-parameter ratio = 17.1.

The title compound, $[Cu_2\{SC(NH_2)NHNH_2\}_6]I_2$, was obtained by the reaction of CuI and thiosemicarbazide (TSCZ) in acetonitrile. Each Cu^I ion is coordinated by four S atoms of the TSCZ ligands, forming a tetrahedral geometry. Centrosymmetric dimers are formed by two coordination tetrahedra sharing a common edge, with a Cu···Cu distance of 2.8236 (14) Å. The I^- ion does not have any direct interaction with the metal. The crystal structure is stabilized by weak N—H···N, N—H···S and N—H···I hydrogen bonds, forming a three-dimensional network structure.

Related literature

For similar structures, see: Chattopadhyay *et al.* (1991); Burrows *et al.* (2004); Tong *et al.* (2000).



Experimental

Crystal data

$[Cu_2(CH_5N_3S)_6]I_2$ M_r = 927.72
Monoclinic, $C2/c$
a = 16.437 (4) Å
b = 8.4174 (15) Å
c = 22.546 (4) Å
β = 105.385 (5)°
V = 3007.6 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.92 mm^{-1}
T = 273 (2) K
0.45 × 0.37 × 0.23 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.272, T_{max} = 0.466
(expected range = 0.237–0.406)
7573 measured reflections
2636 independent reflections
2135 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.106
S = 1.01
2636 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.99 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N9^{i}	0.86	2.44	3.219 (6)	152
N1—H1B···S2	0.86	2.73	3.426 (5)	140
N2—H2···I1^{ii}	0.86	2.80	3.526 (5)	143
N3—H3B···S3^{iii}	0.86	2.95	3.692 (5)	145
N4—H4A···S2^{iv}	0.86	2.72	3.446 (4)	142
N4—H4B···N6^{v}	0.86	2.38	3.225 (6)	167
N5—H5···S1	0.86	2.79	3.424 (4)	132
N6—H6A···N4^{iv}	0.86	2.52	3.225 (6)	139
N7—H7B···I1^{vi}	0.86	3.15	3.620 (4)	117
N8—H8···S1^{vii}	0.86	2.68	3.499 (4)	161
N9—H9B···I1^{viii}	0.86	2.98	3.608 (5)	132

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2195).

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Di-μ-thiosemicarbazide-κ^4S:S-bis[bis(thiosemicarbazide-κS)copper(I)] diiodide

Li Jia, Shou-Xin Ma and Da-Cheng Li

S1. Comment

In previous papers, thiosemicarbazide (TSCZ) has two coordination types; one is as a monodentate S-donor (Chattopadhyay *et al.*, 1991; Tong *et al.*, 2000), the other is as an S,*N*-chelating agent (Burrows *et al.*, 2004). We report the synthesis and the structure of a TSCZ complex of cuprous iodide, (I), in which TSCZ acts as a monodentate S-donor. As shown in Fig. 1, each Cu^{I} atom is in a tetrahedral coordination environment. It is coordinated by two bridging TSCZ ligands and two terminal TSCZ ligands. The Cu—S distances are 2.3118 (14), 2.3192 (13), 2.4098 (13) and 2.4136 (14) Å, which are longer than 2.2266 (1) Å for $[Cu(SC(NH_2)NHNH_2)Cl_2]$ (Chattopadhyay *et al.*, 1991). The bond lengths for S=C are 1.730 (5), 1.726 (4) and 1.702 (5) Å; the corresponding bond length in $[Cu(SC(NH_2)NHNH_2)Cl_2]$ is 1.717 (4)Å (Chattopadhyay *et al.*, 1991).

In the crystal structure, hydrogen bonds are involved. Intramolecular N—H···S interactions appear to influence the conformation of the dimer, while intermolecular N—H···N, N—H···S and N—H···I interactions link the dimers and anions into a three-dimensional network structure (Fig. 2).

S2. Experimental

CuI (0.19 g 1 mmol) and thiosemicarbazide (0.18 g, 2 mmol) were refluxed in 10 ml acetonitrile for 24 h, and a colorless solution formed. After filtration, the solution was allowed to evaporate slowly, and crystals suitable for X-ray diffraction were obtained after several days.

S3. Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, with N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N).

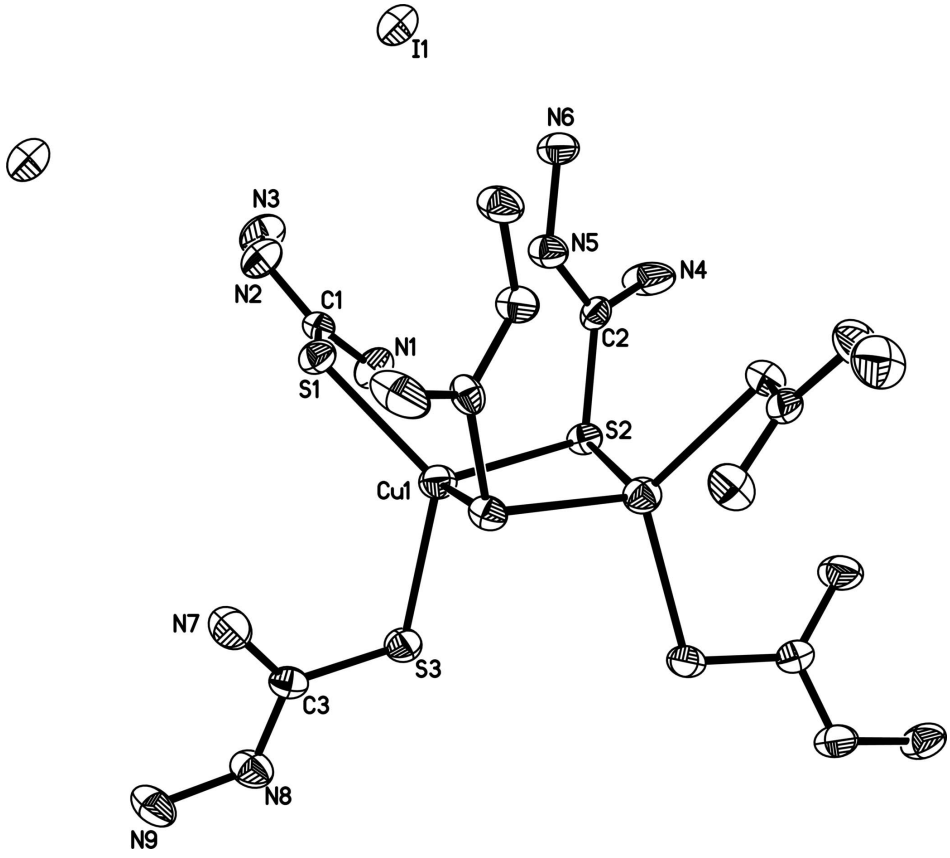

Figure 1

The molecular structure of (I), with atom labels and 40% probability displacement ellipsoids for non-H atoms. [Symmetry code for unlabeled atoms: 1 - *x*, *y*, 3/2 - *z*.]

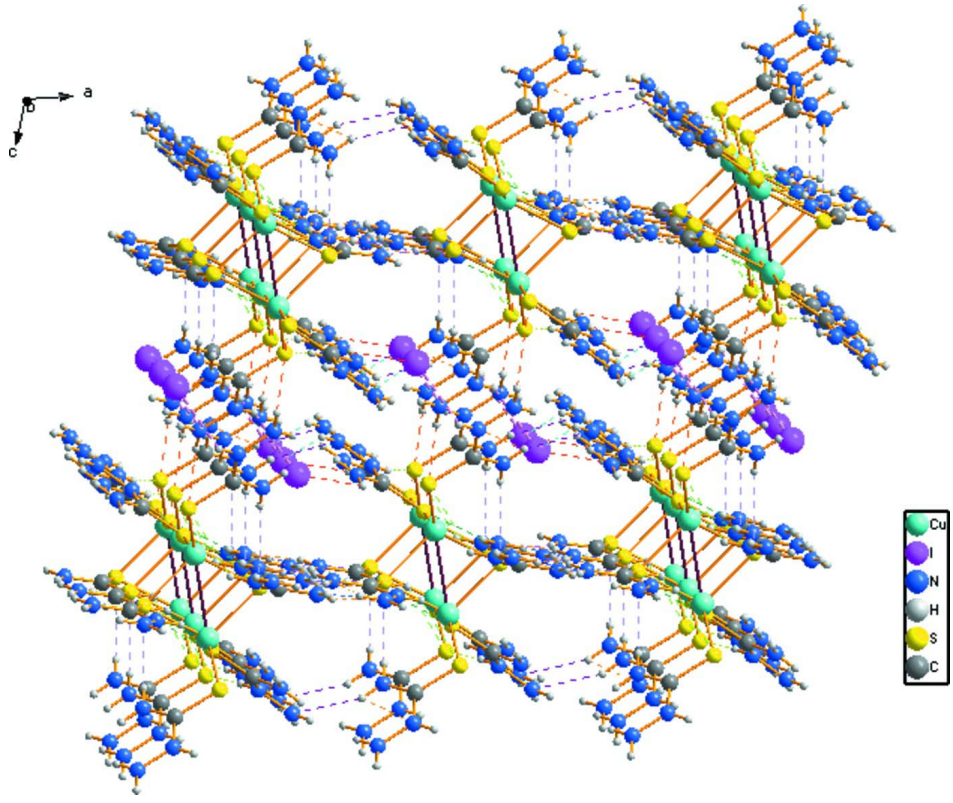

Figure 2

Three-dimensional network structure of the title complex.

Di-μ-thiosemicarbazide-κ^4S:S-bis[bis(thiosemicarbazide-κS)copper(I)] diiodide

Crystal data

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$M_r = 927.72$
Monoclinic, $C2/c$
$a = 16.437\ (4)$ Å
$b = 8.4174\ (15)$ Å
$c = 22.546\ (4)$ Å
$\beta = 105.385\ (5)°$
$V = 3007.6\ (10)$ Å^3
$Z = 4$
$F(000) = 1808$
$D_x = 2.049$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4159 reflections
$\theta = 2.6–27.8°$
$\mu = 3.92$ mm^{-1}
$T = 273$ K
Block, colorless
0.45 × 0.37 × 0.23 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.272$, $T_{max} = 0.466$
7573 measured reflections
2636 independent reflections
2135 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
$h = -19\rightarrow19$
$k = -10\rightarrow9$
$l = -26\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.106$
$S = 1.01$
2636 reflections
154 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 7.7455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.46872 (4)	−0.07773 (6)	0.68532 (3)	0.04027 (19)
I1	0.65686 (2)	0.58550 (4)	0.582631 (19)	0.05668 (17)
N1	0.5760 (3)	0.0278 (5)	0.5883 (2)	0.0488 (11)
H1A	0.6145	0.0354	0.5689	0.059*
H1B	0.5809	−0.0413	0.6171	0.059*
N2	0.5046 (3)	0.2253 (5)	0.5297 (2)	0.0543 (12)
H2	0.4618	0.2879	0.5195	0.065*
N3	0.5685 (3)	0.2350 (6)	0.4990 (2)	0.0617 (13)
H3A	0.6114	0.1726	0.5091	0.074*
H3B	0.5647	0.3034	0.4700	0.074*
N4	0.7280 (3)	0.1713 (5)	0.7543 (3)	0.0783 (19)
H4A	0.7449	0.2677	0.7531	0.094*
H4B	0.7643	0.0957	0.7643	0.094*
N5	0.5934 (2)	0.2573 (4)	0.7257 (2)	0.0407 (9)
H5	0.5402	0.2375	0.7164	0.049*
N6	0.6214 (3)	0.4144 (4)	0.7244 (2)	0.0467 (11)
H6A	0.6746	0.4347	0.7336	0.056*
H6B	0.5854	0.4904	0.7144	0.056*
N7	0.2933 (3)	−0.2581 (5)	0.5981 (2)	0.0601 (14)
H7A	0.2449	−0.2781	0.5732	0.072*
H7B	0.3049	−0.1636	0.6124	0.072*
N8	0.3286 (3)	−0.5151 (5)	0.5913 (2)	0.0492 (11)
H8	0.3644	−0.5916	0.6010	0.059*
N9	0.2482 (3)	−0.5449 (5)	0.5508 (2)	0.0555 (12)
H9A	0.2120	−0.4692	0.5409	0.067*

H9B	0.2355	−0.6387	0.5362	0.067*
S1	0.42975 (7)	0.11539 (13)	0.61021 (6)	0.0390 (3)
S2	0.61502 (7)	−0.05460 (13)	0.74208 (6)	0.0344 (3)
S3	0.44805 (8)	−0.34566 (13)	0.66223 (6)	0.0423 (3)
C1	0.5100 (3)	0.1217 (5)	0.5738 (2)	0.0361 (10)
C2	0.6478 (3)	0.1399 (5)	0.7409 (2)	0.0347 (10)
C3	0.3498 (3)	−0.3726 (5)	0.6145 (2)	0.0360 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0445 (4)	0.0355 (3)	0.0419 (4)	−0.0033 (2)	0.0134 (3)	0.0014 (3)
I1	0.0626 (3)	0.0556 (3)	0.0537 (3)	0.01216 (16)	0.0185 (2)	0.01200 (17)
N1	0.049 (3)	0.056 (2)	0.047 (3)	0.011 (2)	0.023 (2)	0.011 (2)
N2	0.065 (3)	0.052 (3)	0.049 (3)	0.006 (2)	0.020 (2)	0.017 (2)
N3	0.081 (3)	0.063 (3)	0.051 (3)	0.006 (2)	0.035 (3)	0.013 (2)
N4	0.032 (3)	0.043 (3)	0.143 (6)	−0.0066 (19)	−0.006 (3)	0.028 (3)
N5	0.030 (2)	0.0341 (19)	0.057 (3)	−0.0014 (16)	0.0111 (18)	−0.0001 (19)
N6	0.035 (2)	0.032 (2)	0.069 (3)	−0.0013 (15)	0.006 (2)	0.0072 (19)
N7	0.044 (3)	0.041 (2)	0.084 (4)	0.008 (2)	−0.004 (2)	−0.010 (2)
N8	0.046 (2)	0.035 (2)	0.066 (3)	0.0022 (18)	0.013 (2)	−0.010 (2)
N9	0.046 (3)	0.045 (2)	0.073 (4)	−0.0051 (19)	0.010 (2)	−0.020 (2)
S1	0.0362 (6)	0.0352 (6)	0.0458 (8)	0.0042 (5)	0.0110 (5)	0.0067 (5)
S2	0.0296 (6)	0.0322 (5)	0.0427 (7)	0.0013 (4)	0.0118 (5)	0.0042 (5)
S3	0.0418 (7)	0.0307 (6)	0.0511 (8)	0.0054 (5)	0.0064 (6)	−0.0008 (5)
C1	0.044 (3)	0.028 (2)	0.034 (3)	−0.0051 (19)	0.006 (2)	−0.001 (2)
C2	0.031 (2)	0.038 (2)	0.034 (3)	−0.0014 (19)	0.007 (2)	0.009 (2)
C3	0.040 (3)	0.032 (2)	0.041 (3)	−0.0030 (19)	0.019 (2)	−0.002 (2)

Geometric parameters (Å, º)

Cu1—S1	2.3118 (14)	N5—N6	1.404 (5)
Cu1—S3	2.3192 (13)	N5—H5	0.860
Cu1—S2^{i}	2.4098 (13)	N6—H6A	0.860
Cu1—S2	2.4136 (14)	N6—H6B	0.860
Cu1—Cu1^{i}	2.8236 (14)	N7—C3	1.321 (6)
N1—C1	1.312 (6)	N7—H7A	0.860
N1—H1A	0.860	N7—H7B	0.860
N1—H1B	0.860	N8—C3	1.318 (6)
N2—C1	1.307 (6)	N8—N9	1.415 (6)
N2—N3	1.405 (6)	N8—H8	0.860
N2—H2	0.860	N9—H9A	0.860
N3—H3A	0.860	N9—H9B	0.860
N3—H3B	0.860	S1—C1	1.730 (5)
N4—C2	1.300 (6)	S2—C2	1.726 (4)
N4—H4A	0.860	S2—Cu1^{i}	2.4098 (13)
N4—H4B	0.860	S3—C3	1.702 (5)
N5—C2	1.315 (6)		

S1—Cu1—S3	121.59 (6)	N5—N6—H6B	120.0
S1—Cu1—S2^{i}	110.09 (5)	H6A—N6—H6B	120.0
S3—Cu1—S2^{i}	98.91 (5)	C3—N7—H7A	120.0
S1—Cu1—S2	112.03 (5)	C3—N7—H7B	120.0
S3—Cu1—S2	105.28 (5)	H7A—N7—H7B	120.0
S2^{i}—Cu1—S2	107.55 (4)	C3—N8—N9	121.4 (4)
S1—Cu1—Cu1^{i}	135.30 (4)	C3—N8—H8	119.3
S3—Cu1—Cu1^{i}	102.91 (4)	N9—N8—H8	119.3
S2^{i}—Cu1—Cu1^{i}	54.23 (4)	N8—N9—H9A	120.0
S2—Cu1—Cu1^{i}	54.11 (4)	N8—N9—H9B	120.0
C1—N1—H1A	120.0	H9A—N9—H9B	120.0
C1—N1—H1B	120.0	C1—S1—Cu1	105.77 (16)
H1A—N1—H1B	120.0	C2—S2—Cu1^{i}	108.92 (16)
C1—N2—N3	120.4 (4)	C2—S2—Cu1	109.82 (16)
C1—N2—H2	119.8	Cu1^{i}—S2—Cu1	71.66 (4)
N3—N2—H2	119.8	C3—S3—Cu1	109.23 (15)
N2—N3—H3A	120.0	N2—C1—N1	118.4 (5)
N2—N3—H3B	120.0	N2—C1—S1	118.4 (4)
H3A—N3—H3B	120.0	N1—C1—S1	123.2 (4)
C2—N4—H4A	120.0	N4—C2—N5	119.0 (4)
C2—N4—H4B	120.0	N4—C2—S2	119.4 (4)
H4A—N4—H4B	120.0	N5—C2—S2	121.6 (3)
C2—N5—N6	120.6 (4)	N8—C3—N7	117.4 (5)
C2—N5—H5	119.7	N8—C3—S3	118.6 (4)
N6—N5—H5	119.7	N7—C3—S3	124.0 (4)
N5—N6—H6A	120.0		

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N9^{ii}	0.86	2.44	3.219 (6)	152
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Symmetry codes: (ii) $x+1/2, y+1/2, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $-x+3/2, y+1/2, -z+3/2$; (vi) $-x+3/2, y-1/2, -z+3/2$; (vii) $x-1/2, y-1/2, z$; (viii) $x, y-1, z$; (ix) $x-1/2, y-3/2, z$.