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# (2,2′-Bipyridine-$\kappa^2N,N'$)bis(5-thioxo-1,5-dihydro-1,3,4-thiadiazole-3-thiolato-$\kappa S$)-zinc(II)

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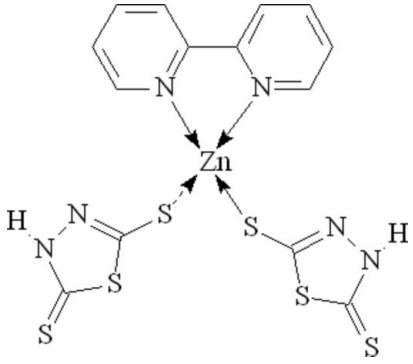
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.027; $wR$ factor = 0.072; data-to-parameter ratio = 15.2.

In the crystal structure of the title compound, $[Zn(C_2HN_2S_3)_2(C_{10}H_8N_2)]$, a twofold rotation axis passes through the Zn atom and the midpoint of the C—C bond linking the two pyridine rings. The $Zn^{II}$ atom is located on a $2_1$ axis and is coordinated by two thiolate S atoms of different 5-thioxo-1,5-dihydro-1,3,4-thiadiazole-3-thiolate ligands and two N atoms of a 2,2′-bipyridine ligand in a tetrahedral geometry, with a Zn—S distance of 2.3204 (8) Å and a Zn—N distance of 2.061 (2) Å. In addition, mononuclear molecules are linked together to form a one-dimensional chain by N—H···S hydrogen bonds.

## Related literature

For related crystal structures, see: Bats (1976); Li *et al.* (2005); Mura *et al.* (1985); Qiu *et al.* (2006); Tannai *et al.* (2003, 2005, 2006); Tzeng *et al.* (2007). For related literature, see: Ma *et al.* (2004*a*,*b*).




## Experimental

### Crystal data

$[Zn(C_2HN_2S_3)_2(C_{10}H_8N_2)]$
$M_r$ = 520.01
Monoclinic, $C2/c$
$a$ = 16.265 (5) Å
$b$ = 8.459 (3) Å
$c$ = 15.140 (5) Å
$\beta$ = 94.459 (5)°
$V$ = 2076.8 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.80 mm$^{-1}$
$T$ = 293 (2) K
0.20 × 0.20 × 0.18 mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.898, $T_{max}$ = 1.000
(expected range = 0.650–0.724)
5362 measured reflections
1926 independent reflections
1519 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.072
$S$ = 1.02
1926 reflections
127 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.32 e Å$^{-3}$

**Table 1**
Selected bond angles (°).

| | | | |
|---|---|---|---|
| N3—Zn1—N3$^{i}$ | 80.43 (13) | S2—Zn1—S2$^{i}$ | 117.86 (4) |
| N3—Zn1—S2 | 106.31 (6) | C2—S2—Zn1 | 96.01 (8) |
| N3$^{i}$—Zn1—S2 | 120.49 (6) | | |

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—H1···S3$^{ii}$ | 0.892 (10) | 2.399 (11) | 3.280 (2) | 169 (2) |

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2375).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2381-m2382 [ **doi:10.1107/S160053680704010X** ]

# (2,2'-Bipyridine-$\kappa^2N,N'$)bis(5-thioxo-1,5-dihydro-1,3,4-thiadiazole-3-thiolato-$\kappa S$)zinc(II)

**X.-L. Zhang, Y.-E. Qiu, C.-L. Zhang and B.-W. Xin**

## Comment

The structures of 2,5-dimercapto-1,3,4-thiodiazole (Bats, 1976) and some metal-complexes of it (Li *et al.*, 2005; Mura *et al.*, 1985; Ma *et al.*, 2004*a*,b; Qiu *et al.*, 2006; Tannai *et al.*, 2003, 2005, 2006 and Tzeng *et al.*, 2007) have been reported. In these complexes, different co-ligands were used and the 2,5-dimercapto-1,3,4-thiodiazole shows different coordination modes and valences. Herein, we report its neutral $Zn^{II}$ complex with 2,2'-bipyridine as a co-ligand, $[Zn(C_{10}H_8N_2)(C_2HN_2S_3)_2]$, (I).

As shown in Fig. 1, the title compound (I) has a mononuclear structure, in which the center Zn(II) atom lies on a $2_1$ axis and is four-coordinated by two thiolato S donors of distinct 1,3,4-thiadiazole-3*H*-5-thione-2-thiolato ligands and two N atoms of one 2,2'-bipyridine. The related bond distances and angles are listed in Table 1. The 2,2'-bipyridine molecule is also of $2_1$ axis symmetry and chelates to $Zn^{II}$. Each 1,3,4-thiadiazole-3*H*-5-thione-2-thiolato ligand located on a general crystallographic position coordinates to one $Zn^{II}$ atom by one S atom. The dihedral angle between two 1,3,4-thiadiazole-3*H*-5-thione-2-thiolato ligands is 94.2 (2) °. In addition, in the crystal structure of (I) such mononuclear molecules were connected with each other to form a one-dimensional chain (Fig. 2) by N—H···S hydrogen bonds (Table 2).

## Experimental

A mixture of $ZnCl_2$ (27 mg, 0.2 mmol), 2,5-dimercapto-1,3,4-thiodiazole (60 mg, 0.4 mmol), 2,2'-bipyridine (31 mg, 0.2 mmol) and NaOH (16 mg, 0.4 mmol) in 10 ml of water was placed in a Teflon-lined stainless-steel Parr bomb that was heated at 423 K for 36 h. Yellowy crystals were collected after the bomb allowed to cool to room temperature during a period of 24 h. Yield, 35%. FT—IR (KBr pellets, $cm^{-1}$): 3437 s, 2866 s, 1493 s, 1445*m*, 1272 s, 1123*m*, 1034 s, 764*m*, 709 s.

## Refinement

The C-bound H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 Å and $U_{iso}$(H) = 1.2 $U_{eq}$(C). The N-bound H atom was located in Fourier difference maps and refined isotropically, with an N—H distance restraint of 0.90 (1) Å.

## Figures

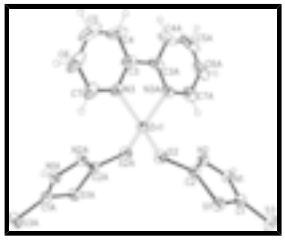

Fig. 1. The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A) $1-x, y, 3/2+z$]

Fig. 2. A view of the title molecules linked together to form a one-dimensional chain by N—H···S hydrogen bonds.

**(2,2'-Bipyridine-κ$^2$*N*,*N*')bis(5-thioxo-1,5-dihydro-1,3,4- thiadiazole-3-thiolato-κ*S*)zinc(II)**

*Crystal data*

| | |
|---|---|
| $[Zn(C_2HN_2S_3)_2(C_{10}H_8N_2)]$ | $F_{000}$ = 1048 |
| $M_r$ = 520.01 | $D_x$ = 1.663 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -C 2yc | Cell parameters from 2398 reflections |
| *a* = 16.265 (5) Å | θ = 2.5–27.1º |
| *b* = 8.459 (3) Å | μ = 1.80 mm$^{-1}$ |
| *c* = 15.140 (5) Å | *T* = 293 (2) K |
| β = 94.459 (5)º | Block, yellow |
| *V* = 2076.8 (11) Å$^3$ | 0.20 × 0.20 × 0.18 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART 1000 CCD area-detector diffractometer | 1926 independent reflections |
| Radiation source: fine-focus sealed tube | 1519 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.025 |
| *T* = 293(2) K | $\theta_{max}$ = 25.5º |
| φ and ω scans | $\theta_{min}$ = 2.5º |
| Absorption correction: multi-scan (SADABS; Bruker, 1998) | *h* = −18→19 |
| $T_{min}$ = 0.898, $T_{max}$ = 1.000 | *k* = −10→8 |
| 5362 measured reflections | *l* = −12→18 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.028 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.072 | $w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.8193P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.02 | $(\Delta/\sigma)_{max} < 0.001$ |
| 1926 reflections | $\Delta\rho_{max}$ = 0.23 e Å$^{-3}$ |
| 127 parameters | $\Delta\rho_{min}$ = −0.32 e Å$^{-3}$ |
| 1 restraint | Extinction correction: none |

Primary atom site location: structure-invariant direct methods

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.5000 | 0.57996 (4) | 0.7500 | 0.03989 (14) |
| S1 | 0.49436 (4) | 0.21183 (8) | 0.51132 (4) | 0.04524 (19) |
| S2 | 0.57283 (4) | 0.43839 (8) | 0.65050 (5) | 0.04630 (19) |
| S3 | 0.33274 (4) | 0.09665 (10) | 0.41761 (5) | 0.0593 (2) |
| N1 | 0.35803 (12) | 0.3258 (2) | 0.54091 (13) | 0.0417 (5) |
| N2 | 0.41163 (12) | 0.4103 (2) | 0.59810 (13) | 0.0418 (5) |
| N3 | 0.57461 (13) | 0.7660 (3) | 0.79288 (14) | 0.0479 (5) |
| C1 | 0.38719 (14) | 0.2145 (3) | 0.48950 (15) | 0.0409 (6) |
| C2 | 0.48732 (14) | 0.3636 (3) | 0.58965 (15) | 0.0372 (5) |
| C3 | 0.54328 (18) | 0.9097 (3) | 0.77031 (17) | 0.0541 (7) |
| C4 | 0.5915 (3) | 1.0451 (4) | 0.7835 (2) | 0.0848 (13) |
| H4A | 0.5696 | 1.1437 | 0.7679 | 0.102* |
| C5 | 0.6712 (3) | 1.0331 (6) | 0.8194 (3) | 0.1046 (17) |
| H5A | 0.7039 | 1.1228 | 0.8274 | 0.126* |
| C6 | 0.7020 (2) | 0.8877 (5) | 0.8433 (2) | 0.0919 (13) |
| H6A | 0.7556 | 0.8778 | 0.8687 | 0.110* |
| C7 | 0.65260 (18) | 0.7551 (4) | 0.8292 (2) | 0.0656 (8) |
| H7A | 0.6739 | 0.6563 | 0.8453 | 0.079* |
| H1 | 0.3047 (7) | 0.348 (3) | 0.5441 (16) | 0.046 (7)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.0350 (2) | 0.0344 (2) | 0.0502 (3) | 0.000 | 0.00271 (18) | 0.000 |
| S1 | 0.0391 (4) | 0.0501 (4) | 0.0471 (4) | 0.0024 (3) | 0.0076 (3) | −0.0099 (3) |
| S2 | 0.0332 (3) | 0.0495 (4) | 0.0561 (4) | −0.0012 (3) | 0.0031 (3) | −0.0094 (3) |
| S3 | 0.0474 (4) | 0.0766 (5) | 0.0535 (4) | −0.0024 (4) | 0.0024 (3) | −0.0284 (4) |
| N1 | 0.0336 (11) | 0.0468 (12) | 0.0445 (12) | 0.0021 (10) | 0.0024 (9) | −0.0077 (10) |
| N2 | 0.0384 (11) | 0.0428 (12) | 0.0439 (12) | −0.0014 (9) | 0.0023 (9) | −0.0082 (9) |
| N3 | 0.0484 (13) | 0.0469 (13) | 0.0497 (13) | −0.0125 (10) | 0.0118 (10) | −0.0061 (10) |
| C1 | 0.0392 (13) | 0.0466 (14) | 0.0375 (13) | −0.0013 (11) | 0.0065 (10) | −0.0026 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0378 (13) | 0.0364 (12) | 0.0377 (13) | −0.0003 (11) | 0.0053 (10) | 0.0010 (11) |
| C3 | 0.0796 (19) | 0.0387 (14) | 0.0485 (16) | −0.0105 (13) | 0.0337 (15) | −0.0096 (12) |
| C4 | 0.143 (4) | 0.0446 (17) | 0.075 (2) | −0.034 (2) | 0.062 (3) | −0.0226 (16) |
| C5 | 0.131 (4) | 0.096 (3) | 0.095 (3) | −0.075 (3) | 0.064 (3) | −0.054 (3) |
| C6 | 0.072 (2) | 0.126 (3) | 0.081 (3) | −0.058 (2) | 0.026 (2) | −0.042 (2) |
| C7 | 0.0495 (17) | 0.078 (2) | 0.070 (2) | −0.0203 (16) | 0.0100 (15) | −0.0136 (17) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Zn1—N3 | 2.061 (2) | N3—C7 | 1.346 (3) |
| Zn1—N3$^{i}$ | 2.061 (2) | N3—C3 | 1.351 (3) |
| Zn1—S2 | 2.3204 (8) | C3—C4 | 1.394 (4) |
| Zn1—S2$^{i}$ | 2.3204 (8) | C3—C3$^{i}$ | 1.492 (6) |
| S1—C1 | 1.749 (2) | C4—C5 | 1.368 (6) |
| S1—C2 | 1.758 (2) | C4—H4A | 0.9300 |
| S2—C2 | 1.727 (2) | C5—C6 | 1.366 (6) |
| S3—C1 | 1.677 (2) | C5—H5A | 0.9300 |
| N1—C1 | 1.332 (3) | C6—C7 | 1.386 (4) |
| N1—N2 | 1.379 (3) | C6—H6A | 0.9300 |
| N1—H1 | 0.892 (10) | C7—H7A | 0.9300 |
| N2—C2 | 1.308 (3) | | |
| N3—Zn1—N3$^{i}$ | 80.43 (13) | N2—C2—S2 | 124.21 (18) |
| N3—Zn1—S2 | 106.31 (6) | N2—C2—S1 | 113.41 (17) |
| N3$^{i}$—Zn1—S2 | 120.49 (6) | S2—C2—S1 | 122.36 (14) |
| N3—Zn1—S2$^{i}$ | 120.49 (6) | N3—C3—C4 | 120.4 (3) |
| N3$^{i}$—Zn1—S2$^{i}$ | 106.31 (6) | N3—C3—C3$^{i}$ | 115.44 (15) |
| S2—Zn1—S2$^{i}$ | 117.86 (4) | C4—C3—C3$^{i}$ | 124.2 (2) |
| C1—S1—C2 | 90.09 (11) | C5—C4—C3 | 120.0 (4) |
| C2—S2—Zn1 | 96.01 (8) | C5—C4—H4A | 120.0 |
| C1—N1—N2 | 119.8 (2) | C3—C4—H4A | 120.0 |
| C1—N1—H1 | 125.1 (16) | C6—C5—C4 | 119.3 (3) |
| N2—N1—H1 | 115.1 (16) | C6—C5—H5A | 120.4 |
| C2—N2—N1 | 109.64 (19) | C4—C5—H5A | 120.4 |
| C7—N3—C3 | 119.3 (2) | C5—C6—C7 | 119.4 (4) |
| C7—N3—Zn1 | 126.1 (2) | C5—C6—H6A | 120.3 |
| C3—N3—Zn1 | 113.94 (18) | C7—C6—H6A | 120.3 |
| N1—C1—S3 | 127.25 (19) | N3—C7—C6 | 121.6 (3) |
| N1—C1—S1 | 107.09 (17) | N3—C7—H7A | 119.2 |
| S3—C1—S1 | 125.66 (15) | C6—C7—H7A | 119.2 |
| N3—Zn1—S2—C2 | −152.67 (11) | Zn1—S2—C2—N2 | 10.1 (2) |
| N3$^{i}$—Zn1—S2—C2 | −64.32 (11) | Zn1—S2—C2—S1 | −168.23 (13) |
| S2$^{i}$—Zn1—S2—C2 | 68.51 (8) | C1—S1—C2—N2 | 0.18 (19) |
| C1—N1—N2—C2 | 1.1 (3) | C1—S1—C2—S2 | 178.71 (16) |
| N3$^{i}$—Zn1—N3—C7 | −173.8 (3) | C7—N3—C3—C4 | 0.8 (4) |
| S2—Zn1—N3—C7 | −54.7 (2) | Zn1—N3—C3—C4 | −170.8 (2) |
| S2$^{i}$—Zn1—N3—C7 | 82.8 (2) | C7—N3—C3—C3$^{i}$ | 179.4 (3) |

| | | | |
|---|---|---|---|
| $N3^{i}$—Zn1—N3—C3 | −2.92 (13) | Zn1—N3—C3—$C3^{i}$ | 7.8 (3) |
| S2—Zn1—N3—C3 | 116.21 (17) | N3—C3—C4—C5 | 0.1 (4) |
| $S2^{i}$—Zn1—N3—C3 | −106.29 (17) | $C3^{i}$—C3—C4—C5 | −178.4 (3) |
| N2—N1—C1—S3 | 178.57 (18) | C3—C4—C5—C6 | −1.1 (5) |
| N2—N1—C1—S1 | −0.9 (3) | C4—C5—C6—C7 | 1.2 (5) |
| C2—S1—C1—N1 | 0.40 (18) | C3—N3—C7—C6 | −0.7 (4) |
| C2—S1—C1—S3 | −179.12 (18) | Zn1—N3—C7—C6 | 169.8 (2) |
| N1—N2—C2—S2 | −179.18 (17) | C5—C6—C7—N3 | −0.3 (5) |
| N1—N2—C2—S1 | −0.7 (2) | | |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···$S3^{ii}$ | 0.892 (10) | 2.399 (11) | 3.280 (2) | 169 (2) |

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

**Fig. 1**

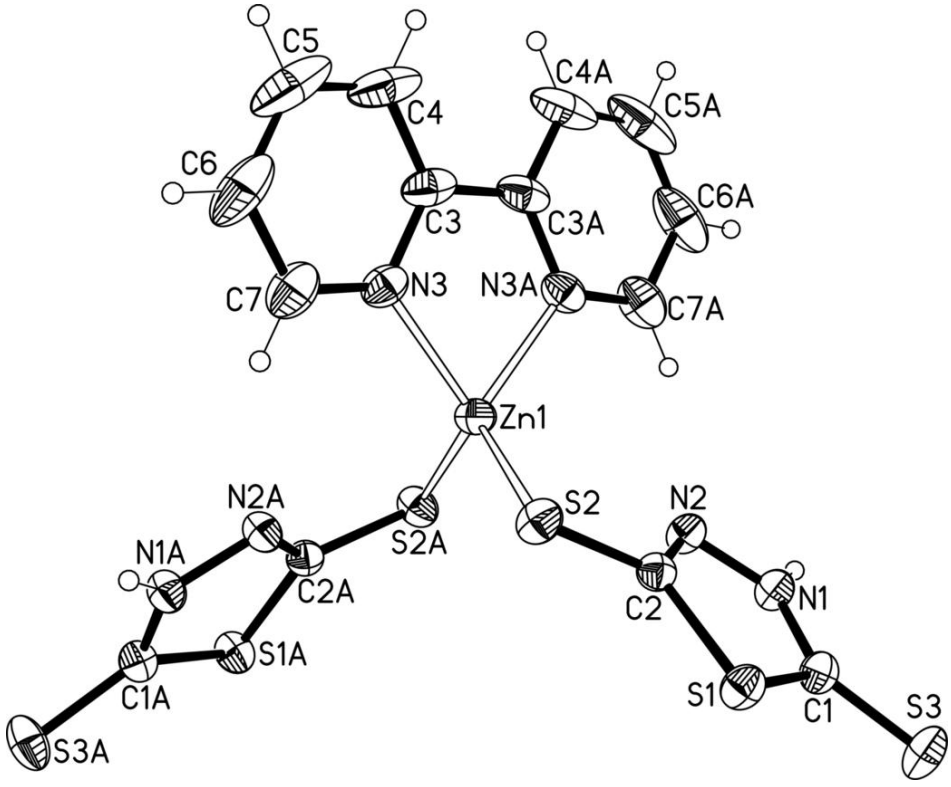
C5
C4
C4A
C5A
C6
C3
C3A
C6A
C7
N3
N3A
C7A
Zn1
N2A
S2A
S2
N2
N1A
C2A
C2
N1
S1A
S1
C1A
C1
S3
S3A

**Fig. 2**