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Bis[1-(4-iodobenzyl)pyridinium] bis(maleonitriledithiolato)nickelate(II)

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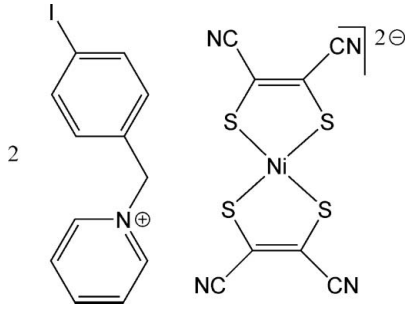
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.036; wR factor = 0.072; data-to-parameter ratio = 20.7.

In the crystal structure of the title complex, $(C_{12}H_{11}IN)_2[Ni(C_4N_2S_2)_2]$, the $[Ni(mnt)_2]^{2-}$ anion (mnt is maleonitriledithiolate) lies on an inversion center and possesses a square-planar geometry. Strong S···I stacking interactions are observed between anions and cations in the crystal structure, with S···I separations of 3.3863 (9) Å.

Related literature

For related literature, see: Coomber *et al.* (1996); Davison & Holm (1967); Gama *et al.* (1992); Kawamura *et al.* (1997); Ren *et al.* (2002, 2004, 2005, 2006); Xie *et al.* (2002, 2003).



Experimental

Crystal data

$(C_{12}H_{11}IN)_2[Ni(C_4N_2S_2)_2]$
M_r = 931.31
Monoclinic, $P2_1/n$
a = 12.7723 (16) Å
b = 10.4489 (13) Å
c = 13.7585 (17) Å
β = 105.889 (2)°
V = 1766.0 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.57 mm^{-1}
T = 293 (2) K
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.459, T_{max} = 0.776
10837 measured reflections
4243 independent reflections
2438 reflections with $I > 2\sigma(I)$
R_{int} = 0.070

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.072
S = 0.82
4243 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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, 2000); 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: BH2107).

References

Bruker (2000). *SMART*, *SAINT*, *SADABS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Coomber, A. T., Beljonne, D., Friend, R. H., Bredas, J. L., Charlton, A., Robertson, N., Underhill, A. E., Kurmoo, M. & Day, P. (1996). *Nature (London)*, **380**, 144–146.
Davison, A. & Holm, R. H. (1967). *Inorg. Synth.* **10**, 8–26.
Gama, V., Henriques, R. T., Bonfait, G., Almeida, M., Meetsma, A., Van Smaalen, S. & De Boer, J. L. (1992). *J. Am. Chem. Soc.* **114**, 1986–1989.
Kawamura, T., Miyazaki, Y. & Sorai, M. (1997). *Chem. Phys. Lett.* **273**, 435–438.
Ren, X. M., Akutagawa, T., Nishihara, S., Nakamura, T., Fujita, W. & Awaga, K. (2005). *J. Phys. Chem. B*, **109**, 16610–16615.
Ren, X., Meng, Q., Song, Y., Lu, C., Hu, C. & Chen, X. (2002). *Inorg. Chem.* **41**, 5686–5692.
Ren, X. M., Nishihara, S., Akutagawa, T., Noro, S., Nakamura, T., Fujita, M. & Awaga, T. (2006). *Chem. Phys. Lett.* **418**, 423–427.
Ren, X. M., Okudera, H., Kremer, R. K., Song, Y., He, C., Meng, Q. J. & Wu, P. H. (2004). *Inorg. Chem.* **43**, 2569–2576.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.
Xie, J., Ren, X., He, C., Song, Y., Meng, Q., Kremer, R. K. & Yao, Y. (2003). *Chem. Phys. Lett.* **369**, 41–48.

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supplementary materials

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Bis[1-(4-iodobenzyl)pyridinium] bis(maleonitriledithiolato)nickelate(II)

H. Zhou and X.-M. Ren

Comment

Some charge transfer salts with their cations and anions packed in segregated stacks exhibit unusual properties in magnetism and conductivity (Gama *et al.*, 1992; Coomber *et al.*, 1996; Kawamura *et al.*, 1997; Ren *et al.*, 2002; Xie *et al.*, 2002, 2003). In our previous studies, benzylpyridinium derivatives were employed as the countercations of $[M(\mathrm{mnt})_2]^-$ ions (M = Ni^{3+} or Pt^{3+}; mnt^{2-} = maleonitriledithiolate) to prepare a series of compounds with segregated stacks displaying magnetic transitions (Ren *et al.*, 2002, 2004, 2005, 2006; Xie *et al.*, 2002, 2003).

Although all compounds exhibit similar structural features at room temperature, with the anions stacked in columns, the hysteresis loop in the plot of magnetic susceptibility *vs*. temperature was only observed in a compound that possesses obvious S···I interactions between anion and cations (Ren *et al.*, 2006). In order to gain more information about the relationship between intermolecular interactions and magnetic properties, we are designing a series of $[M(\mathrm{mnt})_2]^{2-}$ and $[M(\mathrm{mnt})_2]^-$ anions (M = Ni and Pt), and investigate their crystal structures.

In the crystal of (I), the asymmetric unit consists of one cation placed on a general position and one-half $[Ni(mnt)_2]^{2-}$ dianion lying on an inversion center (Fig. 1). The anionic moiety possesses a square-planar geometry, and the Ni^{II} ion coincides with an inversion center. The Ni—S bond lengths are 2.1629 (8) and 2.1739 (9) Å, and the bond angle within the chelate ring is 91.85 (3)°. The cation adopts a conformation in which the benzene and pyridine rings make dihedral angles of 57.4 (3) and 59.8 (3)° with the reference plane N3/C10/C11, respectively. Benzene ring makes a dihedral angle of 84.95 (11)° with the pyridine ring.

Short contacts between S atoms of anions and I atoms of symmetry related cations are observed (Fig. 2). The $S1\cdots I1^{i}$ separation of 3.3863 (9) Å [symmetry code: (i) $-1/2-x, -1/2+y, 1/2-z$) is small compared to the sum of van der Waals radii of S (1.80 Å) and I (2.04 Å).

Experimental

Disodium maleonitriledithiolate (Na_2mnt) was prepared following a procedure found in the literature (Davison & Holm, 1967). 1-(4'-iodobenzyl)pyridinium bromide was prepared by reacting 4-iodobenzylchlorine with 1.5 equivalent of pyridine in refluxing acetone for 4 h. The white microcrystalline product formed was filtered, washed with acetone and diethyl ether, and dried in vacuum (yield: *ca*. 80%). $NiCl_2{\cdot}6H_2O$, Na_2mnt and 1-(4'-iodobenzyl)pyridinium bromide (molar ratio 1:2:2) were mixed in water. The red precipitated product, (I), was separated, washed with water and then dissolved in a minimum amount of MeCN. This MeCN solution of (I) was kept at 277 K for 6 days, affording single crystals of (I) suitable for structure analysis. Crystals were separated, washed with Et_2O and dried in vacuum (Yield: *ca*. 70%).

Refinement

All H atoms were placed in calculated positions and refined using a riding model, with C—H bond lengths constrained to 0.93 (aromatic CH) or 0.97 Å (methylene CH_2) and $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Figures

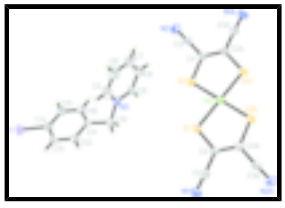


Fig. 1. : The structure of complex (I), showing 30% probability displacement ellipsoids with numbering scheme [symmetry code: (A) 1 − *x*, 1 − *y*, 1 − *z*].

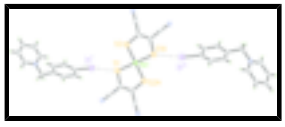


Fig. 2. : The S···I stacking interactions between anion and cations [symmetry codes: (i) −0.5 − *x*, −1/2 + *y*, 0.5 − *z*; (ii) 1.5 + *x*, 1.5 − *y*, −1/2 + *z*; (A) 1 − *x*, 1 − *y*, 1 − *z*].

bis[1-(4-iodobenzyl)pyridinium] bis(1,2-dicyanoethane-1,2-dithiolato-κ^2*S*,*S*')nickelate(II)

Crystal data

$(C_{12}H_{11}IN)_2[Ni(C_4N_2S_2)_2]$	$Z = 2$
$M_r = 931.31$	$F_{000} = 908$
Monoclinic, $P2_1/n$	$D_x = 1.751$ Mg m^{-3}
Hall symbol: -P 2yn	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.7723$ (16) Å	$\theta = 2.5$–25.1°
$b = 10.4489$ (13) Å	$\mu = 2.57$ mm^{-1}
$c = 13.7585$ (17) Å	$T = 293$ (2) K
$\beta = 105.889$ (2)°	Block, red
$V = 1766.0$ (4) Å^3	0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	4243 independent reflections
Radiation source: fine-focus sealed tube	2438 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.070$
$T = 293$(2) K	$\theta_{max} = 28.3$°
φ and ω scans	$\theta_{min} = 1.9$°
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -16 \rightarrow 11$
$T_{min} = 0.459$, $T_{max} = 0.776$	$k = -13 \rightarrow 13$
10837 measured reflections	$l = -16 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.82$	$(\Delta/\sigma)_{max} = 0.002$
4243 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.69$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.5000	0.04272 (15)
S1	0.35566 (6)	0.39970 (8)	0.51129 (7)	0.0500 (2)
S2	0.39653 (7)	0.66191 (8)	0.43750 (7)	0.0572 (2)
I1	−0.58920 (2)	0.84666 (3)	0.104948 (19)	0.07120 (12)
N1	0.2621 (2)	0.0847 (3)	0.5759 (2)	0.0675 (9)
N2	0.4103 (2)	1.0011 (3)	0.3686 (2)	0.0642 (8)
N3	−0.0135 (2)	0.7533 (3)	0.2672 (2)	0.0531 (7)
C1	0.3260 (3)	0.1552 (3)	0.5657 (2)	0.0481 (8)
C2	0.4039 (2)	0.2484 (3)	0.5530 (2)	0.0417 (7)
C3	0.4463 (3)	0.9027 (3)	0.3929 (2)	0.0473 (8)
C4	0.4887 (2)	0.7777 (3)	0.4259 (2)	0.0419 (7)
C5	−0.0119 (4)	0.8025 (4)	0.3575 (3)	0.0818 (12)
H5A	−0.0656	0.7792	0.3882	0.098*
C6	0.0671 (4)	0.8860 (5)	0.4047 (3)	0.0906 (15)
H6A	0.0679	0.9183	0.4679	0.109*
C7	0.1447 (3)	0.9225 (4)	0.3605 (3)	0.0791 (12)
H7A	0.1991	0.9795	0.3927	0.095*
C8	0.1415 (3)	0.8744 (4)	0.2686 (3)	0.0770 (12)
H8A	0.1933	0.8994	0.2363	0.092*
C9	0.0622 (3)	0.7889 (4)	0.2229 (3)	0.0619 (10)
H9A	0.0612	0.7554	0.1601	0.074*
C10	−0.0975 (3)	0.6579 (3)	0.2174 (3)	0.0736 (12)
H10A	−0.0902	0.5827	0.2601	0.088*
H10B	−0.0848	0.6318	0.1539	0.088*
C11	−0.2118 (3)	0.7089 (3)	0.1972 (3)	0.0529 (9)
C12	−0.2872 (3)	0.6445 (3)	0.2336 (3)	0.0577 (9)
H12A	−0.2661	0.5729	0.2743	0.069*
C13	−0.3943 (3)	0.6858 (3)	0.2098 (3)	0.0552 (9)
H13A	−0.4447	0.6429	0.2354	0.066*
C14	−0.4253 (3)	0.7893 (3)	0.1491 (2)	0.0505 (8)

C15	−0.3494 (3)	0.8555 (3)	0.1138 (3)	0.0631 (10)
H15A	−0.3701	0.9279	0.0738	0.076*
C16	−0.2438 (3)	0.8144 (3)	0.1377 (3)	0.0623 (10)
H16A	−0.1931	0.8586	0.1132	0.075*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0384 (3)	0.0356 (3)	0.0544 (3)	−0.0057 (3)	0.0131 (3)	0.0053 (3)
S1	0.0388 (5)	0.0393 (5)	0.0727 (6)	−0.0041 (4)	0.0165 (4)	0.0090 (4)
S2	0.0403 (5)	0.0462 (5)	0.0845 (6)	−0.0026 (4)	0.0161 (5)	0.0166 (5)
I1	0.05189 (17)	0.0832 (2)	0.07392 (19)	0.00774 (13)	0.00940 (13)	−0.00856 (14)
N1	0.062 (2)	0.0524 (19)	0.089 (2)	−0.0197 (16)	0.0215 (17)	0.0109 (17)
N2	0.064 (2)	0.0444 (19)	0.084 (2)	0.0034 (16)	0.0200 (17)	0.0096 (17)
N3	0.0456 (17)	0.0469 (18)	0.0687 (19)	0.0032 (14)	0.0187 (15)	−0.0013 (15)
C1	0.047 (2)	0.044 (2)	0.053 (2)	−0.0009 (16)	0.0123 (16)	0.0025 (16)
C2	0.0430 (19)	0.0344 (17)	0.0502 (18)	−0.0099 (14)	0.0171 (15)	−0.0016 (15)
C3	0.043 (2)	0.046 (2)	0.055 (2)	−0.0091 (17)	0.0169 (16)	−0.0003 (17)
C4	0.0444 (19)	0.0369 (18)	0.0450 (18)	−0.0046 (15)	0.0132 (15)	0.0000 (14)
C5	0.080 (3)	0.103 (4)	0.075 (3)	0.005 (3)	0.042 (3)	0.007 (3)
C6	0.079 (3)	0.126 (4)	0.066 (3)	0.001 (3)	0.018 (3)	−0.031 (3)
C7	0.053 (3)	0.092 (3)	0.083 (3)	−0.001 (2)	0.004 (2)	−0.024 (3)
C8	0.060 (3)	0.097 (3)	0.077 (3)	−0.024 (2)	0.023 (2)	−0.017 (2)
C9	0.054 (2)	0.071 (3)	0.065 (2)	−0.002 (2)	0.024 (2)	−0.012 (2)
C10	0.054 (2)	0.048 (2)	0.124 (3)	−0.0009 (18)	0.033 (2)	−0.013 (2)
C11	0.050 (2)	0.041 (2)	0.071 (2)	−0.0046 (17)	0.0237 (19)	−0.0133 (18)
C12	0.059 (2)	0.043 (2)	0.075 (2)	−0.0022 (18)	0.024 (2)	0.0058 (17)
C13	0.049 (2)	0.054 (2)	0.067 (2)	−0.0093 (18)	0.0249 (19)	−0.0024 (19)
C14	0.047 (2)	0.050 (2)	0.054 (2)	−0.0006 (17)	0.0126 (17)	−0.0078 (17)
C15	0.064 (3)	0.051 (2)	0.073 (2)	0.002 (2)	0.018 (2)	0.0115 (19)
C16	0.065 (3)	0.052 (2)	0.081 (3)	−0.0044 (19)	0.038 (2)	0.006 (2)

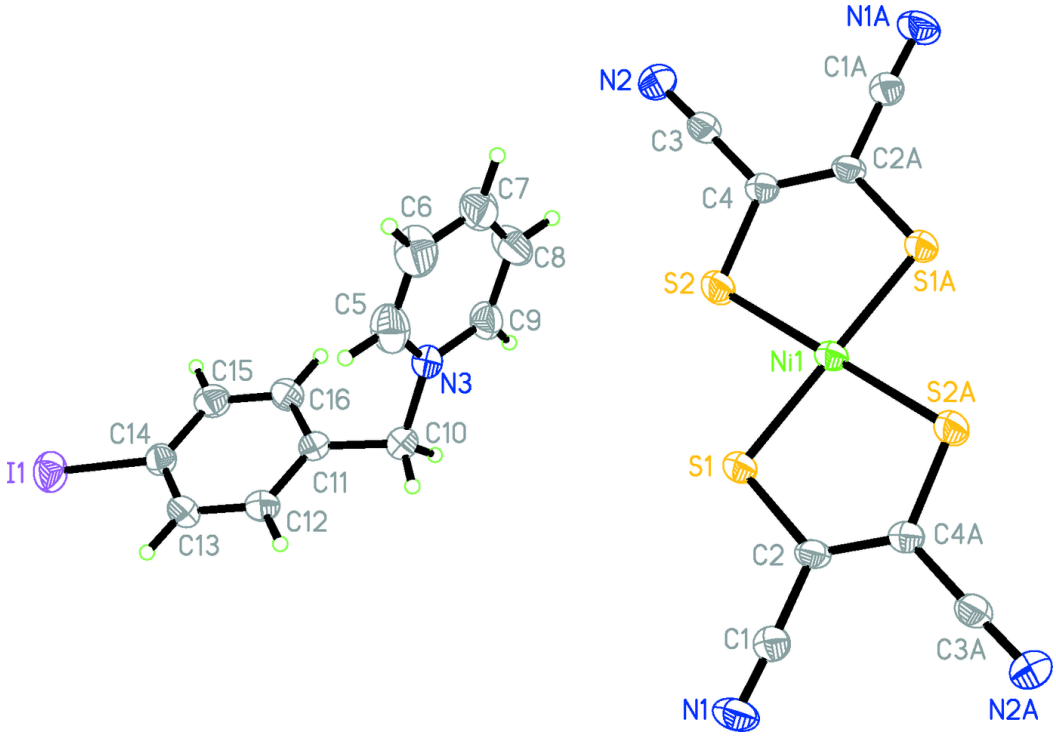
Geometric parameters (Å, °)

Ni1—S1^{i}	2.1629 (8)	C6—H6A	0.9300
Ni1—S1	2.1629 (8)	C7—C8	1.351 (5)
Ni1—S2^{i}	2.1739 (9)	C7—H7A	0.9300
Ni1—S2	2.1739 (9)	C8—C9	1.367 (5)
S1—C2	1.737 (3)	C8—H8A	0.9300
S2—C4	1.725 (3)	C9—H9A	0.9300
I1—C14	2.101 (3)	C10—C11	1.507 (4)
N1—C1	1.136 (4)	C10—H10A	0.9700
N2—C3	1.138 (4)	C10—H10B	0.9700
N3—C9	1.329 (4)	C11—C16	1.367 (5)
N3—C5	1.340 (5)	C11—C12	1.377 (4)
N3—C10	1.487 (4)	C12—C13	1.385 (4)
C1—C2	1.436 (4)	C12—H12A	0.9300
C2—C4^{i}	1.351 (4)	C13—C14	1.357 (4)

C3—C4	1.439 (5)	C13—H13A	0.9300
C4—C2^{i}	1.351 (4)	C14—C15	1.384 (4)
C5—C6	1.358 (6)	C15—C16	1.367 (5)
C5—H5A	0.9300	C15—H15A	0.9300
C6—C7	1.351 (5)	C16—H16A	0.9300
S1^{i}—Ni1—S1	180.0	C7—C8—H8A	119.9
S1^{i}—Ni1—S2^{i}	88.15 (3)	C9—C8—H8A	119.9
S1—Ni1—S2^{i}	91.85 (3)	N3—C9—C8	120.9 (3)
S1^{i}—Ni1—S2	91.85 (3)	N3—C9—H9A	119.6
S1—Ni1—S2	88.15 (3)	C8—C9—H9A	119.6
S2^{i}—Ni1—S2	180.0	N3—C10—C11	112.8 (3)
C2—S1—Ni1	103.46 (10)	N3—C10—H10A	109.0
C4—S2—Ni1	103.07 (11)	C11—C10—H10A	109.0
C9—N3—C5	119.3 (3)	N3—C10—H10B	109.0
C9—N3—C10	120.0 (3)	C11—C10—H10B	109.0
C5—N3—C10	120.7 (3)	H10A—C10—H10B	107.8
N1—C1—C2	177.8 (4)	C16—C11—C12	119.2 (3)
C4^{i}—C2—C1	122.3 (3)	C16—C11—C10	120.8 (3)
C4^{i}—C2—S1	120.1 (2)	C12—C11—C10	119.9 (3)
C1—C2—S1	117.5 (2)	C11—C12—C13	120.4 (3)
N2—C3—C4	177.7 (3)	C11—C12—H12A	119.8
C2^{i}—C4—C3	121.5 (3)	C13—C12—H12A	119.8
C2^{i}—C4—S2	121.2 (2)	C14—C13—C12	119.8 (3)
C3—C4—S2	117.3 (2)	C14—C13—H13A	120.1
N3—C5—C6	120.7 (4)	C12—C13—H13A	120.1
N3—C5—H5A	119.6	C13—C14—C15	120.0 (3)
C6—C5—H5A	119.6	C13—C14—I1	120.4 (3)
C7—C6—C5	120.4 (4)	C15—C14—I1	119.6 (3)
C7—C6—H6A	119.8	C16—C15—C14	119.9 (3)
C5—C6—H6A	119.8	C16—C15—H15A	120.0
C8—C7—C6	118.6 (4)	C14—C15—H15A	120.0
C8—C7—H7A	120.7	C11—C16—C15	120.7 (3)
C6—C7—H7A	120.7	C11—C16—H16A	119.6
C7—C8—C9	120.1 (4)	C15—C16—H16A	119.6

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

Fig. 1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N2A
C7
C6
C8
C5
C9
N3
C15
C16
C14
C10
I1
C11
C12
C13

Fig. 2