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The Crystal Structure of Tetracyanothiophene

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Tetracyanothiophene crystallizes in space group *Pa* with $a=13{\cdot}42$, $b=6{\cdot}56$, $c=7{\cdot}07$ Å, $\beta=137{\cdot}0°$, and two molecules in the unit cell. The structure has been determined from three-dimensional film data and refined with anisotropic thermal parameters using the method of least squares. The molecule has approximate C_{2v} symmetry with average distances: S–C, 1·71 Å; C=C, 1·37 Å; C–C, 1·40 Å; C–C_N, 1·41 Å; C≡N, 1·17 Å. Intermolecular distances as short as N---C, 2·98 Å, and N---S, 3·22 Å, suggest weak donor–acceptor bonding between molecules.

Introduction and experimental

As a part of a general study of intermolecular interactions between cyanide nitrogen atoms and heavy non-metal atoms, we have determined the crystal structure of tetracyanothiophene. This work was prompted by the discovery by Hazell (1963) of strong intermolecular nitrogen–selenium interactions in $Se(CN)_2$ and by the

Table 1. *Final atomic parameters and standard deviations for tetracyanothiophene from full-matrix anisotropic least-squares refinement*

	$x(10^4\sigma_x)$	$y(10^4\sigma_y)$	$z(10^4\sigma_z)$	Equivalent B
S	0	0·6990 (6)	½	3·56 Å^2
C(2)	0·1058 (16)	0·9089 (20)	0·6211 (31)	3·14
C(3)	0·1849 (15)	0·9124 (22)	0·5622 (28)	3·24
C(4)	0·1530 (17)	0·7415 (20)	0·4077 (34)	2·97
C(5)	0·0583 (16)	0·6161 (21)	0·3629 (30)	3·55
C(22)	0·1133 (21)	1·0643 (35)	0·7657 (44)	6·55
C(33)	0·2783 (22)	1·0611 (29)	0·6384 (40)	5·01
C(44)	0·2152 (20)	0·7089 (28)	0·3088 (32)	4·24
C(55)	0·0032 (16)	0·4216 (23)	0·2128 (31)	3·52
N(2)	0·1195 (27)	1·1951 (34)	0·8856 (52)	8·83
N(3)	0·3559 (20)	1·2063 (36)	0·7120 (37)	6·81
N(4)	0·2743 (22)	0·6697 (35)	0·2541 (37)	8·20
N(5)	−0·0385 (17)	0·2640 (21)	0·0970 (33)	5·87

Thermal coefficients* (× 10^4)

	$\beta_{11}(\sigma\beta_{11})$	$\beta_{22}(\sigma\beta_{22})$	$\beta_{33}(\sigma\beta_{33})$	$\beta_{12}(\sigma\beta_{12})$	$\beta_{13}(\sigma\beta_{13})$	$\beta_{23}(\sigma\beta_{23})$
S	114 (6)	184 (9)	497 (22)	−74 (8)	192 (10)	−149 (16)
C(2)	85 (19)	139 (35)	459 (79)	−44 (21)	149 (36)	−76 (45)
C(3)	73 (19)	201 (40)	230 (65)	9 (25)	65 (30)	−22 (45)
C(4)	113 (21)	132 (41)	354 (71)	40 (22)	155 (35)	18 (41)
C(5)	105 (21)	151 (37)	430 (88)	45 (24)	146 (39)	143 (43)
C(22)	164 (31)	475 (78)	681 (120)	6 (38)	252 (55)	−239 (81)
C(33)	173 (28)	287 (54)	395 (87)	−110 (37)	185 (44)	−106 (57)
C(44)	97 (23)	185 (37)	304 (73)	21 (31)	64 (36)	17 (56)
C(55)	103 (20)	178 (40)	352 (73)	−30 (24)	126 (34)	−104 (47)
N(2)	318 (40)	444 (62)	1190 (139)	−35 (47)	502 (68)	−201 (97)
N(3)	185 (30)	400 (62)	531 (94)	22 (40)	187 (46)	52 (72)
N(4)	200 (30)	720 (89)	577 (100)	65 (44)	248 (51)	−33 (78)
N(5)	187 (27)	186 (47)	671 (89)	−7 (25)	225 (44)	−3 (50)

* Anisotropic temperature factors are of the form $T=\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$.

apparent isomorphism of $S(CN)_2$ and $Se(CN)_2$. After this work was begun, Dollase (1965) determined the structure of tetracyano-1,4-dithiadiene, which is more closely related to tetracyanothiophene than is sulfur dicyanide, and found no unusual intermolecular nitrogen–sulfur distances but did find several short intermolecular nitrogen–carbon distances.

A sample of tetracyanothiophene containing crystals suitable for X-ray diffraction studies was provided by Drs H. E. Simmons and T. L. Cairns (Simmons, Vest, Blomstrom, Roland & Cairns, 1962). The crystals are colorless needles, elongated along **a**. Weissenberg and precession photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) show the crystals to be monoclinic with dimensions:

$$a = 13{\cdot}42 \pm 0{\cdot}04,\ b = 6{\cdot}56 \pm 0{\cdot}02,\ c = 7{\cdot}07 \pm 0{\cdot}02 \text{ Å}$$
$$\beta = 137{\cdot}0 \pm 0{\cdot}5^\circ\,.$$

This cell is the least skewed cell that leaves the needle direction a crystallographic axis. The systematic extinctions ($h0l$, $h = 2n+1$) indicate the space group to be either Pa or $P2/a$. Packing considerations appear to favor Pa, and this conclusion was confirmed by a positive test for pyroelectricity (Bunn, 1961). The experimental density, by flotation, is $1{\cdot}454 \pm 0{\cdot}005$ g.cm^{-3}. The calculated density, for $Z = 2$, is $1{\cdot}440 \pm 0{\cdot}008$ g.cm^{-3}.

Multiple film Weissenberg data (Cu $K\alpha$ radiation) were collected for $0kl$ through $7kl$ with an approximately cylindrical crystal of diameter 0·133 mm, and for $h0l$ through $h3l$ with an approximately rectangular crystal 0·42 mm × 0·16 mm × 0·11 mm. Intensities were measured by comparison with a series of timed exposures of a selected reflection. There were 490 independent reflections with measurable intensities and 68 more in the same region of reciprocal space with intensities too weak to measure. The latter were included in the subsequent least-squares calculations with F(unobserved) taken as two-thirds the minimum observed value of F. Lorentz, polarization, and absorption corrections were made.* The linear absorption coefficient, μ, for Cu $K\alpha$ radiation, is 29·3 cm^{-1}. The absorption corrections were made for the first crystal with the approximation that the crystal was cylindrical, and for the second using the actual shape and point by point integration.

The absorption corrections as well as all of the following calculations were made with programs supplied by Mr L. W. Finger of the Geology Department of the University of Minnesota and were made on the Control Data 1604 Computer of the Numerical Analysis Center of the University of Minnesota. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962).

* It should be mentioned that the structure was solved from the data without any absorption corrections, and that this solution led to a Fourier map that did not differ greatly from the final structure. However, all attempts to refine this solution by least squares were unsuccessful in that the refinement converged to chemically unreasonable structures that disagreed with the Fourier maps.

Determination and refinement of the structure

The structure was determined in a conventional way from three-dimensional Patterson and Fourier maps. A full-matrix least-squares refinement of the positional parameters determined from the best Fourier map and of anisotropic thermal parameters converged to an r value of 0·0311* and gave an R value of 0·103. The final parameters from the least-squares calculations are given in Table 1. The anisotropic thermal parameters are given in Table 2 as the parameters of the ellipsoids of vibration. The observed and calculated structure factors are given in Table 3.

* $r = \Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4$.
$R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

The numerator of r was the function refined. The weights used were: $w = (10{\cdot}8/F_o)^4$ for $F_o > 10{\cdot}8$; $w = 1$ for $F_o \le 10{\cdot}8$; $w = \frac{1}{2}$ for F(unobserved). Attempts to refine the data using anisotropic thermal parameters were unsuccessful until five intense reflections were omitted from the refinement. For each of these the observed structure factor was less than the calculated one, presumably due to extinction. The five omitted reflections are shown in parentheses in Table 3.

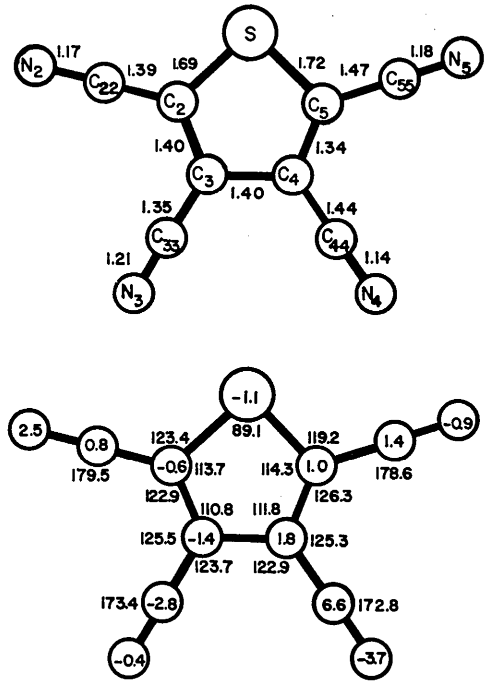

Fig. 1. Top: bond lengths in tetracyanothiophene. The standard deviations in these lengths are 0·02 Å for the S–C distances and 0·02–0·04 Å for the C–C and C–N distances. Bottom: bond angles in degrees, and deviations (in 0·01 Å) from the least-squares plane through the entire molecule (all atoms given equal weight except sulfur, which was weighted four times as large as the other atoms). These deviations (given inside the circles) are of the order of the standard deviations in the calculated positions.

Discussion

Although no crystallographic symmetry is required, the molecule is planar and has C_{2v} symmetry within the experimental error. Bond lengths, bond angles, and deviations from the least-squares plane through the entire molecule are shown in Fig. 1. The packing and intermolecular distances are shown in Fig. 2. The average bond lengths and angles appear normal within experimental error; they are compared in Table 4 to similar dimensions in related molecules.

The intermolecular N---S distances, 3·22 and 3·26 Å, are slightly shorter than the expected van der Waals distance of 3·35 Å. In addition these two nitrogen atoms in the adjacent molecules are approximately coplanar with the molecule so that the sulfur environment is similar to the pseudo square planar arrangement in $S(CN)_2$. However, the N---S distances* in $S(CN)_2$, 2·95 and 2·97 Å, are much shorter than these found here, so that, if the short distances do represent real interactions, they are much weaker in tetracyanothiophene. In tetracyano-1,4-dithiadiene, TCDT, (Dollase, 1965) there are two N---S distances, 3·322 and 3·332 Å, one to each sulfur atom in the molecule, which are just at the van der Waals distance of 3·35 Å, and seven more N---S distances between 3·4 and 3·8 Å. There

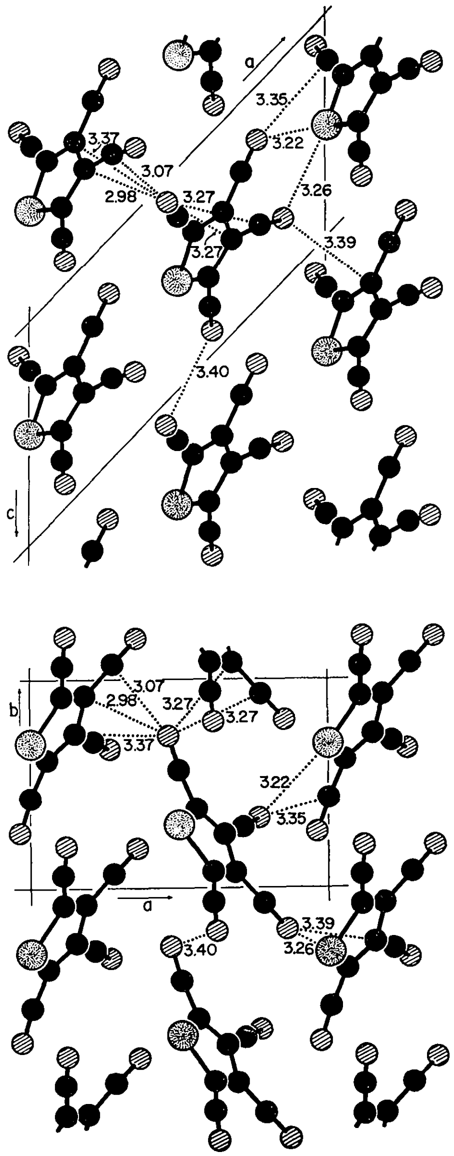

Fig. 2. The crystal structure of tetracyanothiophene. Top: view along **b**. Bottom: view along **c**. Intermolecular distances in Å are given on the Figures.

Table 2. *Parameters for the ellipsoids of vibration*

	r.m.s. amplitude of vibration	Angles with crystallographic axis *a*	*b*	*c*
S	0·15 Å	68°	39°	86°
	0·20	157	76	28
	0·28	83	125	62
C(2)	0·14	58	42	97
	0·20	144	54	54
	0·25	104	109	37
C(3)	0·16	76	86	62
	0·20	119	29	67
	0·24	147	119	38
C(4)	0·14	57	147	115
	0·20	69	74	151
	0·23	41	62	104
C(5)	0·13	90	34	113
	0·22	24	77	116
	0·26	66	121	144
C(22)	0·17	47	127	141
	0·27	54	82	84
	0·39	115	142	52
C(33)	0·18	72	46	77
	0·22	54	66	155
	0·33	139	54	69
C(44)	0·17	72	118	68
	0·20	89	23	76
	0·30	162	96	26
C(55)	0·15	93	42	61
	0·22	143	68	75
	0·25	127	124	34
N(2)	0·25	56	136	134
	0·34	34	58	118
	0·40	86	117	56
N(3)	0·24	84	107	56
	0·30	88	17	81
	0·33	173	90	36
N(4)	0·25	55	104	162
	0·28	137	73	83
	0·41	68	22	107
N(5)	0·20	87	3	91
	0·27	111	88	112
	0·33	159	88	22

* We quote the $S(CN)_2$ results of Emerson (1966) rather than the less accurate results of Linke & Lemmer (1966*a*,*b*). The latter give N–S distances of 2·77 and 2·96 Å.

is no pseudo square planar arrangement around either sulfur atom. Therefore, there is an even weaker suggestion, if there is any at all, that N---S interactions occur in this compound. A determination of the analogous N---Se distances in tetracyano-1,4-diselenadiene and tetracyanoselenophene might settle this point.

Other intermolecular interactions in tetracyanothiophene are indicated by the short N---C distances shown around N(5) in Fig. 2. Here a presumably electron-rich nitrogen atom is near presumably electron-deficient carbon atoms in other thiophene rings and in other CN groups. Similar interactions occur at two of the four nitrogen atoms in tetracyano-1,4-dithiadiene and at all of the nitrogen atoms in tetracyanoethylene (Bekoe & Trueblood, 1960).

The shape of the crystal, elongated in the **a** direction, suggests that the N---S interactions are more important than the N---C interactions in determining the growth of the crystal.

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Table 3. *Observed and calculated structure factors*

H	K	F(O)	F(C)	ALPHA
L=0				
2	0	39.2	37.5	62.7
4	0	15.1	14.9	6.3
6	0	16.1	13.9	-21.1
8	0	8.3	8.8	-11.7
10	0	4.4	6.1	-12.6
0	1	9.2	8.2	0.0
1	1	(20.4)	31.9	-54.3
2	1	24.8	27.8	-207.5
3	1	7.3	7.1	-203.0
4	1	22.7	22.0	-174.1
5	1	17.1	16.5	-54.8
6	1	8.4	8.4	-126.8
7	1	8.9	8.7	-61.8
0	2	(23.7)	40.0	-180.0
1	2	19.0	21.3	-205.5
2	2	12.9	13.2	-203.5
3	2	14.3	14.5	-265.6
4	2	12.7	12.9	-228.3
5	2	8.2	7.6	-177.8
6	2	10.4	10.2	-185.4
7	2	5.1	2.9	88.5
8	2	6.1	5.8	-203.0
0	3	18.5	21.4	0.0
1	3	5.7	4.9	-247.5
2	3	9.9	9.6	13.3
3	3	10.1	10.1	33.7
4	3	19.3	17.9	8.1
5	3	7.3	8.0	-260.9
6	3	4.0	4.4	16.6
7	3	11.7	10.9	82.2
0	4	2.4*	5.4	0.0
1	4	20.9	19.8	-59.7
2	4	7.9	7.2	-73.9
3	4	8.3	8.6	-70.7
4	4	8.3	8.6	-75.3
5	4	11.4	12.8	-97.8
6	4	6.4	7.2	-45.7
7	4	5.4	5.1	-76.4
0	5	13.5	13.5	-180.0
1	5	4.4*	3.1	83.0
2	5	6.8	5.3	-127.6
3	5	8.4	8.1	-267.7
4	5	9.6	9.6	-217.7
5	5	4.8	4.1	-165.7
6	5	5.3	5.4	-207.1
7	5	2.9*	1.1	-239.3
0	6	6.8	8.2	-180.0
1	6	7.6	7.1	-227.9
2	6	5.0	3.4	-82.4
3	6	4.4	3.8	67.6
4	6	4.1	4.3	65.9
5	6	5.9	5.6	62.0
6	6	3.6	3.4	84.9
7	6	5.4	5.5	76.7
0	7	2.8*	4.0	0.0
2	7	6.6	5.9	-19.4
3	7	5.9	6.0	-107.0
4	7	7.5	7.2	-29.2
6	7	4.3	5.2	-13.2
0	8	4.1	2.7	-180.0
L=1				
0	0	(55.1)	50.0	-184.3
2	0	7.2	7.0	-104.4
-2	0	28.0	29.0	-251.0
4	0	18.9	16.8	-256.4
-4	0	55.5	51.6	-236.7
6	0	12.0	11.4	-171.3
-6	0	14.8	14.2	-224.4
-8	0	3.1*	2.8	-169.8
-10	0	8.6	8.2	-154.3
-12	0	5.4	7.3	-191.2
0	1	(49.4)	46.5	-95.0
1	1	(63.6)	76.7	-256.9
-1	1	19.4	21.3	57.5
2	1	24.7	20.8	1.8
-2	1	1.1*	1.4	43.7
3	1	8.0	8.4	-244.3
-3	1	8.5	9.3	87.7
4	1	8.8	8.0	15.1
-4	1	8.8	8.2	-133.4
5	1	11.8	12.2	79.7
-5	1	20.5	23.2	-223.7
6	1	3.0*	2.3	-263.1
-6	1	8.1	7.0	-9.0
7	1	6.8	6.2	-249.9
-7	1	12.8	12.9	-251.3
-8	1	5.5	5.8	-48.7
-9	1	5.0	5.2	-233.7
0	2	18.3	16.9	-57.6
1	2	16.2	13.7	-100.6
-1	2	7.1	6.6	-54.6
2	2	20.4	18.0	29.9
-2	2	10.8	10.7	80.0
3	2	16.0	15.5	-70.8
-3	2	24.8	32.6	-67.3
4	2	5.4	5.0	-52.5
-4	2	18.7	18.7	-16.0
5	2	10.9	10.4	-53.4
-5	2	7.1	6.3	-158.2
6	2	6.2	5.3	33.2
-6	2	19.1	20.7	1.2
7	2	5.5	5.4	-46.4
-7	2	5.0	5.3	-60.0
-8	2	8.6	9.3	5.6
0	3	24.3	22.5	-216.1
1	3	14.9	15.8	-102.2
-1	3	2.3*	2.1	-117.8
2	3	14.9	14.0	-143.1
-2	3	11.6	11.7	-185.5
3	3	10.6	10.3	-118.2
-3	3	13.8	15.2	-31.2
4	3	8.7	8.7	-157.9
-4	3	10.6	10.9	-193.9
5	3	7.4	8.0	-170.1
-5	3	12.2	12.2	-94.4
6	3	6.5	6.8	-160.0
-6	3	7.2	6.3	-179.5
7	3	7.4	6.6	-121.4
-7	3	8.5	8.3	-62.7
-8	3	7.6	7.6	-195.5
-9	3	4.0*	4.8	-153.9
-10	3	5.7	4.4	-179.1
0	4	2.5*	3.7	54.0
1	4	17.0	15.9	-266.4
-1	4	13.0	11.9	71.6
2	4	2.8*	1.8	-204.2
-2	4	5.8	6.1	-36.2
3	4	2.8*	1.5	-237.5
-3	4	14.9	15.1	85.2
4	4	5.3	4.4	31.7
-4	4	9.7	9.8	-159.9
5	4	10.8	10.2	76.4
-5	4	7.7	7.8	-264.3
6	4	2.8*	3.1	-243.5
-6	4	8.0	8.8	-174.2
-7	4	7.7	7.5	52.5
0	5	12.9	14.1	3.8
-1	5	4.4*	1.2	-214.3
2	5	9.7	8.8	79.6
-2	5	10.1	10.3	-4.5
3	5	2.9*	1.9	-72.6
-3	5	6.1	5.8	-154.9
4	5	2.8*	3.4	-24.3
-4	5	11.4	10.1	19.6
5	5	3.0*	4.5	14.8
-5	5	8.9	8.5	-202.0
6	5	6.7	5.6	-10.0
-6	5	6.8	7.7	5.3
-7	5	3.1*	1.6	-174.6
0	6	3.0*	3.1	-59.5
-1	6	8.6	7.9	-85.1
2	6	6.7	6.0	-173.0
-2	6	11.1	10.0	-118.7
-3	6	10.6	10.7	-60.2
4	6	7.0	6.5	-131.3
-4	6	4.2	4.4	-171.0
5	6	6.2	7.0	-128.0
-5	6	5.7	5.9	-85.3
6	6	4.0	4.4	-95.7
-6	6	4.0	2.9	-153.0
-7	6	5.1	6.4	-71.5
0	7	6.1	6.1	-256.5
2	7	5.1	4.4	-201.8
-2	7	2.8*	2.2	-166.4
-3	7	4.8	4.9	86.3
-4	7	3.6	4.2	-178.5
-6	7	4.1	4.4	-174.2
-7	7	4.0	3.4	64.6
0	8	3.6	3.2	38.1
-2	8	3.8	4.0	24.9
-4	8	4.1	4.9	-12.5
L=2				
0	0	7.2	6.6	-250.5
2	0	26.8	23.8	11.8
-2	0	10.2	8.7	-44.7
4	0	6.6	6.4	-28.0
-4	0	37.7	35.5	68.1
6	0	9.6	8.5	2.4
-6	0	15.7	15.4	10.6
-8	0	3.9	1.1	-129.7
-10	0	7.4	7.9	63.0
-12	0	11.3	11.6	5.6
0	1	14.5	13.1	84.0
1	1	17.8	18.7	-103.9
-1	1	14.9	14.4	-117.4
2	1	9.3	9.1	-151.9
-2	1	13.0	11.7	-99.3
3	1	6.1	6.7	-74.0
-3	1	44.7	46.9	-131.8
4	1	5.0	3.6	-93.1
-4	1	16.9	15.9	17.6
5	1	7.7	8.5	-131.5
-5	1	22.5	24.6	-85.6
6	1	2.8*	.4	-125.6
-6	1	11.0	10.2	-85.1
7	1	6.5	4.7	-72.1
-7	1	11.8	11.4	-96.3
-8	1	7.6	8.1	-128.6
-9	1	9.5	10.9	-74.7
-10	1	5.0	4.8	-222.3
-11	1	12.5	12.2	-74.5
0	2	16.6	15.0	-226.6
1	2	26.8	24.6	35.5
-1	2	7.2	5.1	57.1
2	2	25.7	24.7	-159.8
-2	2	12.4	11.6	-155.3
3	2	12.9	14.2	-244.3
-3	2	4.7	5.1	-220.0
4	2	6.3	5.1	-180.6
-4	2	16.2	15.3	-156.3
5	2	5.3	4.1	-256.4
-5	2	14.9	15.5	-268.2
6	2	7.0	5.7	-222.4
-6	2	16.7	17.1	-153.8
7	2	5.8	4.7	-247.8
-7	2	12.0	12.1	-267.6
-8	2	7.8	7.9	-199.5
-9	2	11.3	11.0	67.8
-10	2	6.2	6.2	-201.3
0	3	8.4	7.4	-18.4
1	3	9.7	9.1	26.2
-1	3	6.2	5.9	-53.3
2	3	13.9	13.2	-3.0
-2	3	20.2	16.5	16.8
3	3	5.9	7.8	-219.6
-3	3	12.9	12.1	-246.4
4	3	5.4	4.3	32.8
-4	3	6.6	6.6	-.2
5	3	5.9	5.2	-51.1
-5	3	18.0	18.0	80.7
6	3	2.8	5.7	11.6
-6	3	8.1	8.5	-17.4
-7	3	7.2	7.0	-254.1
-8	3	9.3	9.7	2.3
-9	3	5.9	5.0	49.6
-10	3	6.5	4.2	-2.6
-11	3	5.7	3.7	-193.4
-12	3	5.0	5.0	-5.1
0	4	5.9	5.4	-50.8
1	4	12.0	11.1	-81.2
-1	4	11.7	10.9	-77.7
2	4	10.2	10.2	15.7
-2	4	7.3	5.2	-262.7
3	4	4.4	3.3	.4
-3	4	10.8	10.0	-106.0
4	4	2.8*	.6	-210.4
-4	4	11.8	10.9	31.3
-5	4	6.6	6.6	-64.0
6	4	2.2*	4.0	-79.8
-6	4	5.1	5.3	19.6
-7	4	11.5	11.4	-102.4
0	5	11.5	12.1	-156.0
-1	5	7.2	7.0	-182.8
2	5	6.2	5.4	-168.5
-2	5	16.7	17.4	-169.2
3	5	4.2	4.6	-231.0
-3	5	4.3	4.3	-139.7
4	5	3.7	4.0	-188.6
-4	5	11.9	11.2	-194.4
-5	5	3.1*	3.1	-91.3
6	5	5.2	5.5	-189.6
-6	5	9.3	10.1	-205.5
-7	5	4.7	3.7	-136.4
0	6	4.4	2.6	-31.3
-1	6	4.8	6.6	-264.1
2	6	6.1	4.9	18.0
-2	6	5.8	4.8	.7
-3	6	8.1	8.1	-263.4
-4	6	5.5	5.2	-44.8
-5	6	8.3	8.4	77.0
-6	6	5.2	3.8	7.8
-7	6	8.0	8.6	87.1
0	7	4.4	3.2	-55.4
2	7	4.3	4.3	-.0
-2	7	5.0	4.4	55.5
-3	7	5.1	5.2	-82.4
-4	7	2.4*	2.3	5.2
-2	8	3.7	4.3	-172.4
-4	8	3.4	3.9	-191.3
L=3				
0	0	5.1	4.9	-132.9
2	0	11.5	11.0	-209.0
-2	0	34.1	33.0	-205.4
4	0	6.3	6.1	-164.6
-4	0	37.3	32.7	-132.2
6	0	5.1	3.9	-189.2
-6	0	24.3	23.6	-177.8
-8	0	22.0	20.9	-173.9
-10	0	15.6	15.2	-144.8
-12	0	14.4	14.1	-179.4
-14	0	4.3	3.4	-203.9
0	1	5.6	5.1	-8.0
1	1	4.3	3.4	.1
-1	1	6.8	7.7	-269.6
2	1	6.5	5.0	2.9
-2	1	8.0	8.8	-263.5
3	1	7.8	9.6	-265.9
-3	1	14.6	14.9	-222.9
4	1	4.2	3.3	66.7
-4	1	12.5	11.7	7.9
-5	1	15.2	15.8	-253.6
6	1	2.0*	1.6	-36.6
-6	1	10.3	9.8	54.2
-7	1	12.9	13.5	37.1
-8	1	10.5	11.2	29.9
-9	1	2.6*	3.9	77.4
-10	1	8.3	8.1	-3.0
-11	1	12.2	13.5	-255.1
-12	1	3.2*	3.1	-36.0
-13	1	4.9	6.7	51.9
0	2	10.0	10.0	-57.4
1	2	10.3	9.0	-145.8
-1	2	3.3*	3.1	-88.2
2	2	7.1	7.7	-25.7
-2	2	16.7	15.2	-18.6
3	2	5.9	6.6	-59.7
-3	2	9.5	7.9	-264.1
4	2	4.1	3.1	46.7
-4	2	20.6	19.4	-13.7
-5	2	7.2	8.2	-81.7
6	2	3.9	3.7	-79.1
-6	2	7.8	7.2	-8.5
-7	2	10.9	10.5	-38.8
-8	2	8.6	8.4	-2.8
-9	2	12.4	12.8	-111.5
-10	2	11.6	11.8	24.2
-11	2	5.3	5.4	-147.1
-12	2	5.6	5.1	-15.0
0	3	5.3	5.3	-165.8
1	3	11.3	11.1	-117.6
-1	3	5.0	3.9	-100.6
2	3	8.3	8.6	-193.3
-2	3	6.7	5.5	-202.4
3	3	12.3	12.0	-41.3
-3	3	9.3	8.6	-37.8
-4	3	10.3	9.1	-142.3
-5	3	12.1	11.7	-71.1
-6	3	15.0	14.2	-174.5
-7	3	5.0	5.0	-116.3
-8	3	12.9	12.0	-179.0
-9	3	9.5	7.2	-99.4
-10	3	3.7*	4.8	-188.9
-11	3	3.8*	3.4	-85.4
-12	3	6.7	6.5	-197.8
0	4	9.4	9.5	-246.2
1	4	7.0	6.9	-229.6
-1	4	14.0	14.8	-241.8
2	4	5.2	5.2	-184.1
-2	4	7.1	7.1	-224.2
3	4	6.0	6.4	80.1
-3	4	13.2	12.9	82.3
-4	4	8.0	7.2	-210.0
5	4	3.3	4.1	-235.4
-5	4	8.9	9.2	76.5
-6	4	5.5	3.9	-213.0
-7	4	10.3	11.0	85.6
0	5	4.7	5.5	22.7
-1	5	4.6*	2.9	-68.8
2	5	6.8	6.4	-39.8
-2	5	9.5	9.8	-10.0
-3	5	2.9*	1.7	-252.0
-4	5	8.2	8.8	-15.0
-5	5	5.5	3.7	-28.9
-6	5	12.7	13.4	-18.3
-7	5	7.5	6.3	-31.6
0	6	2.6*	2.7	-148.9
-1	6	7.8	6.8	-67.1
-3	6	2.8	5.6	-119.9
-4	6	4.2	2.7	71.3
-5	6	5.1	5.6	-99.2
-6	6	2.7*	3.4	-25.3
-7	6	6.7	5.2	-102.1
0	7	3.4	3.7	-206.8
-3	7	3.4	4.3	83.4
-4	7	6.2	5.5	-192.2
-6	7	4.0	5.5	-165.7
L=4				
2	0	5.7	5.2	-75.8
-2	0	13.2	12.2	16.2
4	0	5.7	5.9	2.8
-4	0	11.3	10.7	20.3
-6	0	26.8	24.3	-31.1
-8	0	15.8	14.7	-39.3
-10	0	13.0	13.2	8.8
-12	0	13.7	11.9	-24.6
-14	0	5.1	5.7	-25.0
0	1	4.8	4.7	-192.8
-1	1	10.1	10.4	-92.7
2	1	3.0*	1.9	-191.2
-2	1	4.2	3.5	-8.7
3	1	5.8	5.8	-123.1
-3	1	15.2	15.4	-49.4
4	1	2.0*	.6	-113.5
-4	1	12.6	12.6	-184.7
-5	1	12.4	13.0	-86.1
-6	1	5.1	3.1	-141.5
-7	1	17.3	19.2	-89.9
-8	1	8.9	9.3	-199.0
-9	1	10.2	10.5	-53.2
-10	1	8.1	8.0	-200.7
-11	1	11.6	11.6	-83.0
-12	1	5.4	5.5	-254.1
0	2	5.3	5.0	-196.3
-1	2	3.9*	2.0	-223.5
2	2	4.4	3.8	-212.3
-2	2	5.1	4.4	-93.4
3	2	2.4*	2.5	-190.3
-3	2	5.0	5.2	-214.2
4	2	5.1	4.1	-127.9
-4	2	12.1	10.9	-166.3
-5	2	10.0	10.2	-235.2
-6	2	9.7	9.0	-229.6
-7	2	9.6	9.4	-222.1
-8	2	5.6	4.9	-202.7
-9	2	10.9	11.0	-257.2
-10	2	12.8	11.7	-154.1
-11	2	9.1	8.6	54.2
-12	2	5.5	5.2	-206.7
-13	2	3.3*	1.2	22.9
-14	2	5.3	4.6	-157.8
0	3	5.8	6.0	40.6
1	3	9.6	10.0	54.4
-1	3	10.0	9.9	52.7
2	3	3.0*	2.4	21.2
-2	3	6.4	5.5	-.2
3	3	3.0	3.2	-248.8
-3	3	9.7	8.8	45.7
-4	3	8.7	7.6	5.3
-5	3	7.6	7.0	59.3
-6	3	9.2	8.8	24.6
-7	3	3.0*	1.8	87.5
-8	3	7.6	8.4	11.2
-9	3	15.2	14.3	-240.1
-10	3	10.1	10.1	-5.3
-11	3	6.3	7.2	50.7
-12	3	6.5	6.9	-28.6
-13	3	3.5*	.4	-245.4
0	4	2.9*	3.3	-65.2
-1	4	6.9	6.5	-100.8
-2	4	3.1*	1.7	-40.0
3	4	4.7	7.1	-122.3
-3	4	8.0	8.4	-83.1
-4	4	5.1	4.4	-73.7
-5	4	12.4	13.2	-93.9
-6	4	7.5	8.3	-111.6
-7	4	12.9	12.2	-115.3
0	5	4.6	4.2	-137.9
-2	5	6.8	5.9	-206.3
-3	5	2.9*	1.9	-55.6
-4	5	2.8*	3.2	-172.8
-5	5	3.2*	3.4	-121.2
-6	5	7.0	8.1	-171.6
0	6	3.6	3.2	21.4
-3	6	5.2	6.2	64.7
-4	6	2.5*	2.4	63.9
-5	6	5.6	7.0	88.1
L=5				
-2	0	8.4	9.5	-137.3
-4	0	7.7	6.7	-200.8
-6	0	16.1	17.3	-179.3
-8	0	4.6	4.9	-172.6
-10	0	8.8	9.0	-198.6
-12	0	3.2*	2.6	-179.4
-14	0	5.3	5.2	-182.4
0	1	4.2	2.0	8.1
-2	1	3.1*	1.6	-168.4
-3	1	6.3	7.4	-246.8
-4	1	5.3	5.4	22.3
-5	1	12.3	13.3	69.4
-6	1	2.8*	1.3	-142.3
-7	1	11.5	12.7	70.6
-8	1	2.9*	2.7	8.4
-9	1	9.5	10.5	-262.4
-10	1	5.1	4.6	-16.3
-11	1	9.0	9.6	69.0
-12	1	3.1*	3.9	-101.9
-13	1	6.2	7.2	-263.3
0	2	6.8	6.0	-9.6
2	2	4.2	2.9	-22.4
-2	2	4.7	3.0	-.9
-3	2	8.9	9.2	-78.1
-4	2	8.7	9.1	3.2
-5	2	7.6	6.8	-76.8
-6	2	7.6	7.0	-5.1
-7	2	4.6	4.5	-105.1
-8	2	12.0	12.0	37.1
-9	2	12.7	12.4	-65.4
-10	2	11.2	11.2	-5.8
-11	2	10.3	10.3	-123.9
-12	2	3.4*	4.4	-37.4
-13	2	4.9	2.9	-114.1
-14	2	6.6	4.8	26.3
0	3	2.5*	2.8	-171.8
-2	3	5.4	5.3	-148.7
-3	3	5.1	3.9	-144.4
-4	3	9.1	8.9	-166.3
-5	3	9.2	8.5	-170.3
-6	3	9.4	9.0	-187.9
-7	3	6.4	6.5	-256.5
-8	3	3.7*	2.9	-188.1
-9	3	12.8	11.9	-40.1
-10	3	10.6	8.9	-177.7
-11	3	9.0	8.3	-119.9
-12	3	4.0	5.1	-182.7
-14	3	5.3	4.0	-202.6
0	4	4.3	3.4	-224.5
-2	4	2.8*	1.1	-235.6
-6	4	2.8*	3.6	-269.4
-7	4	6.5	7.3	-268.7
-2	5	5.6	5.0	-6.9
-6	5	5.4	6.0	9.4
L=6				
0	0	1.7*	.8	60.1
-4	0	5.6	7.2	-26.2
-6	0	8.6	8.8	10.5
-8	0	8.9	7.8	5.3
-10	0	8.7	8.8	-29.6
-12	0	8.2	6.5	41.0
-14	0	6.6	7.1	20.5
-16	0	7.8	6.1	21.7
-4	1	5.1	4.1	-141.1
-5	1	7.0	7.1	-100.1
-6	1	5.2	3.0	88.0
-7	1	5.6	5.9	-58.8
-8	1	3.4*	5.5	-107.1
-9	1	10.0	11.1	-113.4
-10	1	3.2*	4.1	-165.7
-11	1	3.2*	3.8	-146.3
-12	1	3.2*	2.6	-190.8
-13	1	4.7	5.1	-76.8
-4	2	6.7	6.9	-207.3
-5	2	6.3	5.9	65.6
-6	2	5.8	4.7	-259.5
-7	2	5.4	5.0	5.9
-8	2	9.5	8.1	-140.7
-9	2	3.6*	4.8	-229.4
-10	2	10.0	10.0	-199.0
-11	2	3.5*	4.7	72.6
-12	2	7.6	7.3	-201.1
-13	2	4.9	4.0	71.4
-4	3	3.9	4.1	19.9
-6	3	4.9	5.4	-6.0
-7	3	3.6*	2.0	-167.7
-8	3	6.7	5.6	-3.1
-9	3	6.0	6.1	-220.9
-10	3	5.9	5.5	-21.8
-11	3	5.7	5.4	82.6
-12	3	3.9	3.0	21.4
-13	3	5.3	3.6	-251.4
-14	3	4.8	3.6	-3.9
-7	4	4.9	5.8	-50.5
L=7				
-8	0	9.2	10.2	-191.6
-10	0	5.4	5.5	-224.3
-12	0	5.7	3.8	-163.0
-14	0	5.6	6.6	-157.1
-16	0	9.0	6.7	-178.0
-12	2	6.1	4.3	7.3
-8	3	5.3	4.3	-164.7
-9	3	5.3	4.8	-102.7
-10	3	6.5	3.5	-166.8
-11	3	6.9	5.8	-113.9
-12	3	3.7	3.8	-189.5
-13	3	3.3*	1.9	-69.7
-14	3	5.7	2.5	-169.0

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Table 4. *Comparison of interatomic distances and angles*

Distance or angle	Compound	Value	Reference
S–C	Tetracyanothiophene	1·71 ± 0·02 Å	(*a*)
	Thiophene	1·714 ± 0·002	(*b*)
	α-Thiophenecarboxylic acid	1·697 ± 0·010	(*c*)
	Thiophthene	1·72 ± 0·013	(*d*)
	Thiophthene	1·74 ± 0·013	(*d*)
	1,4-Dithiadiene	1·78 ± 0·05	(*e*)
	Tetracyano-1,4-dithiadiene	1·755 ± 0·003	(*f*)
C=C	Tetracyanothiophene	1·37 ± 0·02	(*a*)
	Thiophene	1·370 ± 0·002	(*b*)
	α-Thiophenecarboxylic acid	1·362 ± 0·012	(*c*)
	Thiophthene	1·36 ± 0·02	(*d*)
	1,4-Dithiadiene	1·29 ± 0·05	(*e*)
	Tetracyano-1,4-dithiadiene	1·344 ± 0·005	(*f*)
C–C (ring)	Tetracyanothiophene	1·40 ± 0·02	(*a*)
	Thiophene	1·423 ± 0·002	(*b*)
	α-Thiophenecarboxylic acid	1·414 ± 0·011	(*c*)
	Thiophthene	1·41 ± 0·02	(*d*)
C–C (external)	Tetracyanothiophene	1·41 ± 0·04	(*a*)
	Tetracyano-1,4-dithiadiene	1·432 ± 0·012	(*f*)
	sp^2–C to sp–C (normal)	1·42	(*g*)
C≡N	Tetracyanothiophene	1·17 ± 0·03	(*a*)
	Tetracyano-1,4-dithiadiene	1·150 ± 0·007	(*f*)
	R–C≡N (normal)	1·158	(*h*)
C–S–C	Tetracyanothiophene	89·1 ± 0·8°	(*a*)
	Thiophene	92·16 ± 0·10	(*b*)
	α-Thiophenecarboxylic acid	92·0 ± 0·4	(*c*)
S–C–C	Tetracyanothiophene	114·1 ± 1·1	(*a*)
	Thiophene	111·47 ± 0·23	(*b*)
	α-Thiophenecarboxylic acid	111·8 ± 0·6	(*c*)
C–C–C	Tetracyanothiophene	111·4 ± 1·4	(*a*)
	Thiophene	112·45 ± 0·18	(*b*)
	α-Thiophenecarboxylic acid	112·2 ± 0·7	(*c*)
N–S (intermolecular)	Tetracyanothiophene	3·22 ± 0·03 Å	(*a*)
		3·26 ± 0·03	(*a*)
	Tetracyano-1,4-dithiadiene	3·322 ± 0·005	(*f*)
		3·332 ± 0·005	(*f*)
	(plus 7 distances in range)	3·397 – 3·795	(*f*)
	Sulfur dicyanide	2·95 ± 0·02	(*i*)
		2·97 ± 0·02	(*i*)
N–C (intermolecular)	Tetracyanothiophene (7 distances in this range)	2·98 – 3·40	(*a*)
	Tetracyano-1,4-dithiadiene (8 distances in this range)	3·13 – 3·35	(*f*)
	Tetracyanoethylene (6 distances in this range)	3·09 – 3·34	(*j*)

(*a*) This work.
(*b*) Bak, Christensen, Hansen-Nygaard & Rastrup-Anderson.
(*c*) Nardelli, Fava & Giraldi (1962).
(*d*) Cox, Gillot & Jeffrey (1949).
(*e*) Howell, Curtis & Lipscomb (1954).
(*f*) Dollase (1965).
(*g*) Bent (1961).
(*h*) Britton (1967).
(*i*) Emerson (1966).
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The Crystal Structure of Bis(ethylenediamine)copper(II) Fluoroborate

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The crystal structure of bis(ethylenediamine)copper(II) fluoroborate, $Cu(en)_2(BF_4)_2$, has been determined from three-dimensional X-ray diffraction data. Crystals are triclinic with space group $P\bar{1}$ and cell dimensions: $a=7{\cdot}42$, $b=8{\cdot}22$, $c=5{\cdot}92$ Å, $\alpha=100°54'$, $\beta=105°12'$, $\gamma=106°0'$. The structure was refined by Fourier and full-matrix least-squares methods on 978 observed reflexions to $R=15{\cdot}3\%$.
The copper ion has the usual distorted octahedral coordination with four N atoms in an approximately square planar arrangement with Cu–N distances of 2·02 and 2·03 Å, and two F atoms completing the distorted octahedron at the longer distance of 2·56 Å. The ethylenediamine molecules are twisted relative to the plane containing the Cu and N atoms, with one C atom 0·40 Å above the plane, and the other 0·32 Å below the plane. The fluoroborate ions are distorted from tetrahedral symmetry.

Experimental

Violet coloured crystals in the form of platelets elongated in the **c** direction were kindly supplied by Dr. B. J. Hathaway (University of Essex).

For the purposes of X-ray analysis, a crystal of maximum dimensions 0.2 mm was used. Three-dimensional Weissenberg data were collected for the crystal rotating about its *a* and *c* axes, allowing the observations of 978 independent reflexions. Intensities were

Table 1. *Final coordinates and standard deviations*

	x/a	*y/b*	*z/c*	σ(*x/a*)	σ(*y/b*)	σ(*z/c*)
Cu	0·0000	0·0000	0·0000	–	–	–
N(1)	0·0555	0·2454	0·2130	0·002	0·002	0·002
N(2)	0·2729	0·0965	−0·0253	0·002	0·002	0·002
C(1)	0·2740	0·3373	0·2899	0·002	0·002	0·003
C(2)	0·3451	0·2924	0·0666	0·002	0·002	0·003
B	0·7714	0·2046	0·6282	0·003	0·002	0·003
F(1)	0·6649	0·2076	0·7936	0·002	0·002	0·002
F(2)	0·9393	0·3514	0·7186	0·002	0·002	0·002
F(3)	0·6657	0·1990	0·4111	0·002	0·001	0·002
F(4)	0·8281	0·0576	0·6039	0·002	0·001	0·002

Table 2. *Final temperature factor parameters*

	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu		2·32	1·29	2·72	0·57	0·75	0·30
N(1)	5·25 Å^2						
N(2)	5·04						
C(1)	5·39						
C(2)	5·59						
B	5·40						
F(1)		5·96	4·19	7·00	2·62	3·53	2·25
F(2)		5·28	3·09	7·20	0·78	−0·22	1·57
F(3)		4·86	3·32	5·05	2·29	0·35	1·21
F(4)		5·29	3·34	5·58	2·80	2·53	1·98