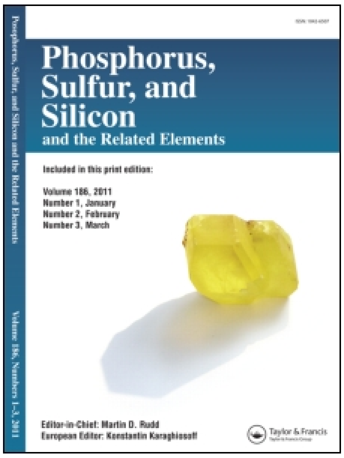

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ORGANIC DITHIOCYANATES—REACTIVITY OF PRODUCTS OF ELECTRONIC TRANSFER AND MATRIX EFFECT

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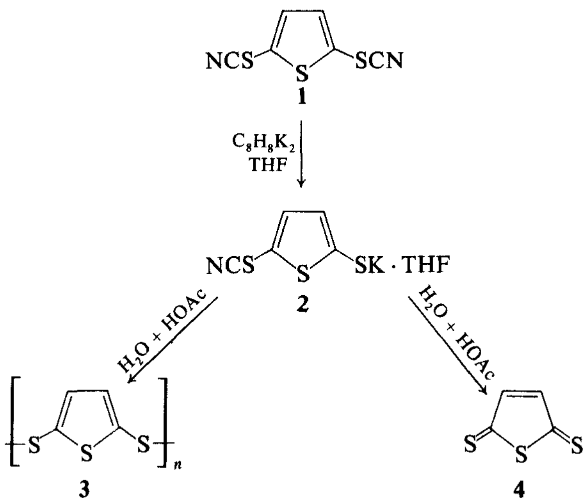
Reaction of 2,5-dithiocyanatothiophene with equimolecular amounts of the dipotassium salt of cyclooctatetraene dianion in THF yields potassium 2-thiocyanato-5-thienylmercaptide. The latter converts to a cyclic tetramer with disulfide bonds—tetra [(thienylen-2,5)disulfide], whose structure was determined by x-ray analysis. In the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6-ether"), the cyclic tetramer formation becomes very difficult and the main product becomes poly [(thienylen-2,5)disulfide] with linear structure.

It is suggested that the potassium cation takes part in forming a transition state as a coordinating center for thienylsulfidic fragments and thus produces the matrix effect.

Examining the reactions of electron transfer from the dipotassium salt of cyclooctatetraene dianion ($C_8H_8K_2$, 1 mole) to 2,5-dithiocyanatothiophene (**1**, 1 mole) in THF solution,[1] we found that the reaction product was potassium 2-thiocyanato-5-thienylmercaptide (**2**). This product is stable in absolute THF, but upon addition of water or aqueous acetic acid to the reaction mixture it transforms to the new crystalline compound containing no nitrogen. At the same time potassium cyanide is formed in quantities approximately corresponding to the initial amounts of dithiocyanatothiophene. The splitting process can be supposed to proceed either by intermolecular reaction of thiocyanato- and mercaptide groups or by intramolecular electron displacement from mercaptide to the thiocyanato group. In the first case a condensation product (**3**) with disulfide bonds could be formed. In the second case trithiomaleic anhydride (**4**) could be formed.

Ebulioscopic molecular weight determination showed the product, formed in 90% yield, had a structure of **3** with $n = 4$.[1] It was necessary to find out whether the condensation of the intermediate **2** led to a linear or a cyclic product. As neither pmr nor mass spectra allowed the elucidation of the structure of the condensation product,[1] we undertook an x-ray study of its crystals grown from a chloroform–toluene mixture.

It turned out that the crystal is built of cyclic



tetrameric molecules with thiophene rings bonded by disulfide bridges (Figure 1). Average bond lengths and bond angles in thiophene rings are equal to S—C 1.73 Å, C=C 1.37 Å, C—C 1.43 Å, C—S—C 92.9°, S—C=C 110.8°, C=C—C 112.9°. These values are in good agreement with those found for thiophene.[2]. The orientation of the thiophene rings is determined on the one hand by a tendency to the maximal molecular compactness and on the other hand by packing conditions in the crystal. Three thiophene rings are rotated in such a way that their sulfur

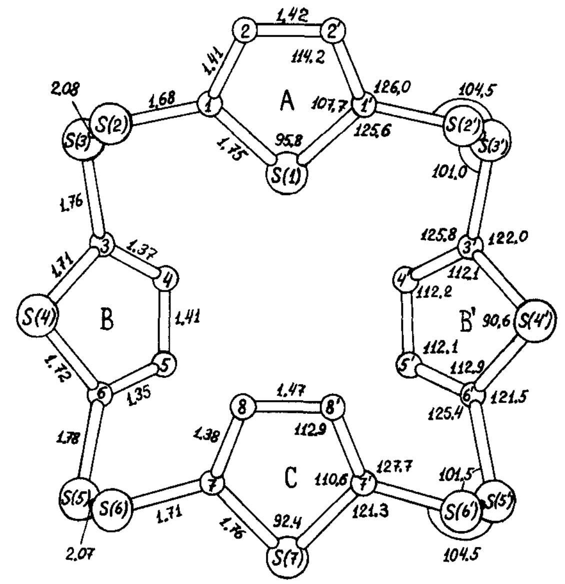


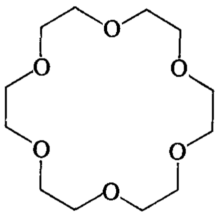
FIGURE 1 Bond lengths and angles in molecule of cyclic tetramer (**3**). Standard deviations in bond lengths S—S 0.008, S—C 0.02, C—C 0.03 Å, in bond angles C—S—S 0.7°, other angles 1.0–1.5°.

atoms are disposed along the outer contour of the macrocycle but the fourth ring is turned with its sulfur inside the macrocycle. Such an orientation indicates definite space strains inside the macrocycle. Angles made by the A, B and C rings (see Figure 1) with a plane crossing the midponts of the disulfide bridges are different: 21.0, 31.8 and 8.8°, respectively. The torsional angle round the $S_{(2)}$—$S_{(3)}$ bond equals 89.2° and corresponds to the most favorable configuration of the disulfide group (the best value of this angle is 90° [3]). The angle at the $S_{(5)}$—$S_{(6)}$ bond is 60.6°, i.e. appreciably diminished from the normal angle, and this decrease leads to contraction of non-bonding intramolecular distances $C_{(6)}\ldots C_{(7)}$ to 3.33 Å, $C_{(6)}\ldots C_{(8)}$ and $C_{(5)}\ldots C_{(8)}$ to 3.43 Å. This geometrical distortion seems to be due to a tendency to close packing of the molecules in the crystal, because the $C_{(7)}$ atom has a short contact distance of 3.36 Å with $C_{(2)}$ of the molecule derived from the reference molecule by an *a*-glide plane. No other intermolecular distances are contracted in respect to the sums of van der Waals radii.

Molecular models of the macrocycle and analysis of the intramolecular distances between non-bonded atoms show that inner strains are not appreciable and that the thiophene rings can rotate around the $C_{(\text{cyclic})}$—$S_{(\text{disulfide})}$ bonds. Indeed, pmr spectra of tetramer solutions at different temperatures indicate the possibility of this rotation. In the temperature range +40 to −40°C, protons of all rings give one sharp singlet with chemical shift $\delta = 7.30$ ppm. It was concluded that the possibility exists of a molecular conformation in which the sulfur atoms of all the thiophene rings are turned inside the macrocycle. Evidently under the action of the dilute acetic acid, potassium 5-thiocyanato-thienyl-2-mercaptide (**2**) transforms only into a cyclic polysulfide with initial inside conformation.

It is, however, clear that a linear product should form more easily than a cyclic one because the former is quite free from inner strains. At the same time, the formation of the cyclic tetramer can show the influence of some specific effects governing the homogeneous process.

In specific experiments we verified the influence of the addition of the following reagents: absolute ethanol (proton donor), absolute acetonitrile (dissociating solvent) and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6-ether") (**5**) as a scavenger of potassium cation.†



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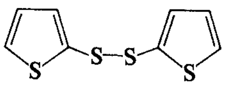

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All of these additives were introduced before an injection of aqueous acetic acid. A change in the reaction course is observed only in the case of the crown ether. The addition of (**5**) was made either before the mixing of **1** with $C_8H_8K_2$ or after this mixing but before injection of water or aqueous acid. The results in the two cases are the same. The presence of crown ether (**5**) resulted in a sharp reduction of the cyclic tetramer yield (to 20%), and the main product was a polymeric tar that contained more than 50% sulfur (from the elemental analysis data). The mass spectrum of this polymeric tar differs from the mass-spectrum of cyclic tetramer (**3**), but is similar to the mass spectrum of 2,2'-dithienyldisulfide (**6**). The mass spectra are described in the experimental. One need only note that the polysulfide molecules yield only nonmolecular fragment ions. The polymer obtained in

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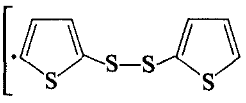
† The polyether diameter for (**5**) is 2.6–3.2 Å.[4] This corresponds well with the size of the potassium cation, for which the double ionic radius is 2.66 Å.[4]

the presence of crown ether yields the fragment ion (**7**) with *m*/*e* = 228. Neither cyclic tetramer (**3**) nor 2,2′-dithienyldisulfide forms these fragments. The data are in agreement with the linear combination (**8**) of fragments in the polymer obtained in the presence of crown ether.



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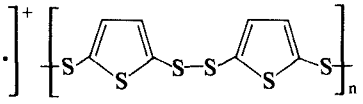

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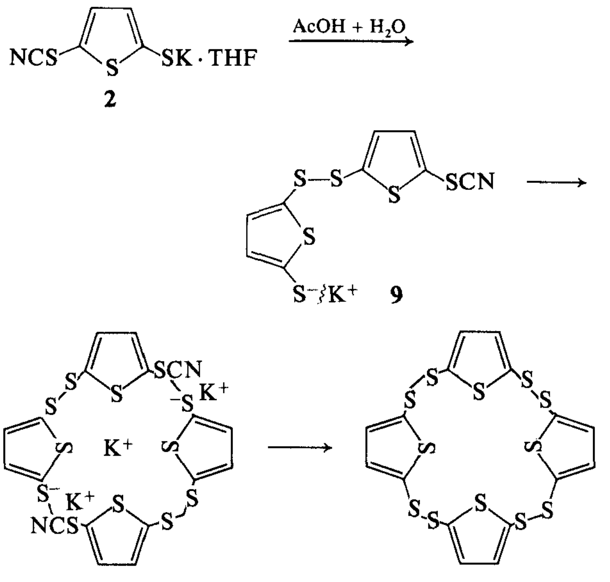
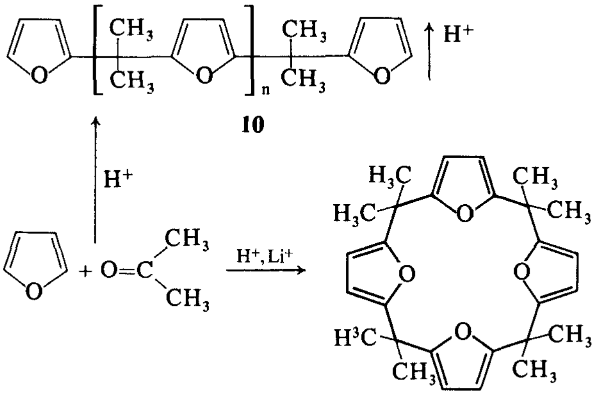
It is important to remember the stability of potassium mercaptide (**2**) in absolute THF. As a solvent THF is non-dissociating. In the presence of the water or aqueous acetic acid in THF, potassium cation is liberated. Further reaction leads to 2-thiocyanato-2′-mercaptido-5,5′-dithienyldisulfide (**9**). Two molecules of disulfide (**9**) are temporarily held by the potassium cation and thereby joined. The cyclic tetramer (**3**) is obtained by this process:



The scheme indicates that in the transformation of potassium 5-thiocyanato-2-thienylmercaptide (**2**) into cyclic tetramer (**3**) the potassium cation plays a decisive role. This cation is able to coordinate the fragments entering the transition state and so produces the matrix effect. In particular such coordination may be carried out with the participation of the sulfur atoms of the thiophene rings. As a result the cyclization, but not the linear condensation, is the preferred process.

In a similar manner the coordination between oxygen atoms of furan rings, on the one hand, and an alkali metal cation, on the other hand, is able to change the course of the furane-acetone condensation.[5]

This reaction takes place in the presence of hydrochloric acid and leads to the linear product (**10**). At the same time a little cyclic tetramer (**11**) is also obtained. Upon addition of lithium perchlorate the yield of the linear product (**10**) is decreased, and the yield of cyclic product (**11**) is increased.



Thus, a metal cation (Li^+, K^+) in these processes can act as a coordinating center and create the matrix effect. Such an effect aids the formation of cyclic but not linear products of the condensation.

The above results may be relevant to the mechanism of certain biochemical conversions that involve redox processes in the presence of biological membranes. It is to be noted that the herbicidal effect of thienylthiocyanates is directly related to interference with electron transport in plants.[6] It is known that biological membranes contain macrocyclic complexing agents (valinomycine, nactines and others); their functions are similar to those of crown ethers.

It is also important to note that after the metallic cation leaves the reaction sphere, the entire situation with regard to electron transfer changes. This affords the opportunity to control the course of many electron reductions for different compounds containing coordinatively active structure elements.

EXPERIMENTAL

1. The splitting of 2,5-dithiocyanato-thiophene (**1**) under the influence of dipotassium cyclooctatetraene ($C_8H_8K_2$) (see also Ref. 1).

The solution of $C_8H_8K_2$ (from 0.66 g, 6.4 mM, of cyclooctatetraene—C_8H_8) in 60 ml of THF was mixed with 1.25 g (6.4 mM) of (**1**) at −40°C and stirred for 1 h. The temperature was allowed to rise to −5°C and then 15 ml of 25% aqueous acetic acid was added. After 12 h the precipitate of cyclic tetramer (**3**) was filtered; the yield 0.83 g, 90% of theory.

2. The splitting of 2,5-dithiocyanatothiophene (**1**) with the aid of $C_8H_8K_2$ in the presence of ethanol and acetonitrile.

To the mixture of $C_8H_8K_2$ (from 0.135 g, 1.3 mM, of C_8H_8) and 0.257 g (1.3 mM) of (**1**) in THF (see the first run) absolute ethanol or acetonitrile (5 ml) was added. The latter reagents were free of atmospheric oxygen. The mixture was stirred for 1 h at −40°C. The temperature was allowed to rise to −5°C and then 5 ml of 25% aqueous acetic acid was poured into the mixture. After 12 h cyclic tetramer (**3**) was filtered. Yields 0.16–0.15 g (85–75% of theory).

3. The splitting of 2,5-dithiocyanatothiophene (**1**) by means of $C_8H_8K_2$ in the presence of 18-crown-6-polyether (**5**).

The solution of $C_8H_8K_2$ (from 0.24 g or 2.32 mM of C_8H_8) in 40 ml of THF was mixed with a solution of 0.46 g (2.32 mM) of (**1**) in 15 ml of THF and then with a solution of 0.6 g (2.32 mM) of crown ether (**5**) in 15 ml of THF at −40°C. In a parallel run, the solution of $C_8H_8K_2$ in THF was flowed into the solution of 2,5-dithiocyanatothiophene and crown ether in THF, all quantities were the same. The results of these parallel runs were the same.

The mixture was stirred for 1 h, the temperature was allowed to rise to −5°C. Then 10 ml of 25% aqueous acetic acid was injected.

After 12 h the solvent was evaporated. The residue was extracted with hot toluene and then by carbon disulfide. The resulting substance was a dark-brown tar slightly soluble in alcohol and chloroform and containing 53.5% sulfur (from the elemental analysis data). This tar was investigated by means of mass spectrometry.

The alcohol–chloroform extract was heated to dryness, leaving 0.05 g of dark-yellow crystals. These crystals became amorphous at 150–160°C, and their PMR spectrum in carbon disulfide solution revealed only one singlet signal with $\delta = 7.30$ ppm. The feature coincides with the δ found for tetramer (**3**). The yield, based on a molecular weight of 580, was equal to 15% of theory.

4. Mass spectra of the cyclic tetramer, tetra(thienylene-2,5)-disulfide, (**3**), and the polymeric substance obtained in the presence of crown ether (**5**).

These mass spectra are different. At the admission temperature of 100°C the cyclic tetramer (**3**) gives $[(C_4H_2S)_5S]^+$, $[(C_4H_2S)_4S_6]^+$, $[(C_4H_2S)_3S_8]^+$, $[(C_4H_2S)_2S_7]^+$, $[(C_4H_2S)S_4]^+$ ions (*m*/*e* 570, 520, 502, 388 and 210, respectively). Besides these, other ions with lesser content of disulfide sulfur are also present, including fragments of the $[(C_4H_2S)_n]^+$ type. 2,2′-Dithienyldisulfide, $(C_4H_3S)_2S_2$ (**6**), investigated as a model compound is disintegrated in a similar manner with a loss of two sulfur atoms, one after another, yielding $[(C_4H_3S)_2S]^+$ and $[(C_4H_3S)_2]^+$ fragments (Figure 2).

Mass spectra of the polymer, prepared in the presence of crown ether (**5**), were observed at the admission temperature of 250 and 300°C. At 30°C no peaks were observed. Peaks observed at 250°C were also reproduced at 300°C, but at 300°C with a higher intensity. These spectra differ from that of the cyclic tetramer (**3**) by an absence of peaks with the above mentioned *m*/*e* values. The mass spectrum of the polymer, which was prepared in the presence of crown ether, contained peaks with *m*/*e* values 344, 342, 230, 228, 198, 197, 192, 178, 177, 166, 133, 131, 117, 116, 115, 101, 89, 88, 87, 76, 73, 70. Thus, in a comparison with 2,2′-dithienyldisulfide (**6**, see Figure 2) peaks are much more numerous and, consequently, the polymer prepared in the presence of crown ether contains dithienyldisulfide links. In this respect the appearance in the mass spectrum of the fragment ion (**7**) with *m*/*e* = 228 is most

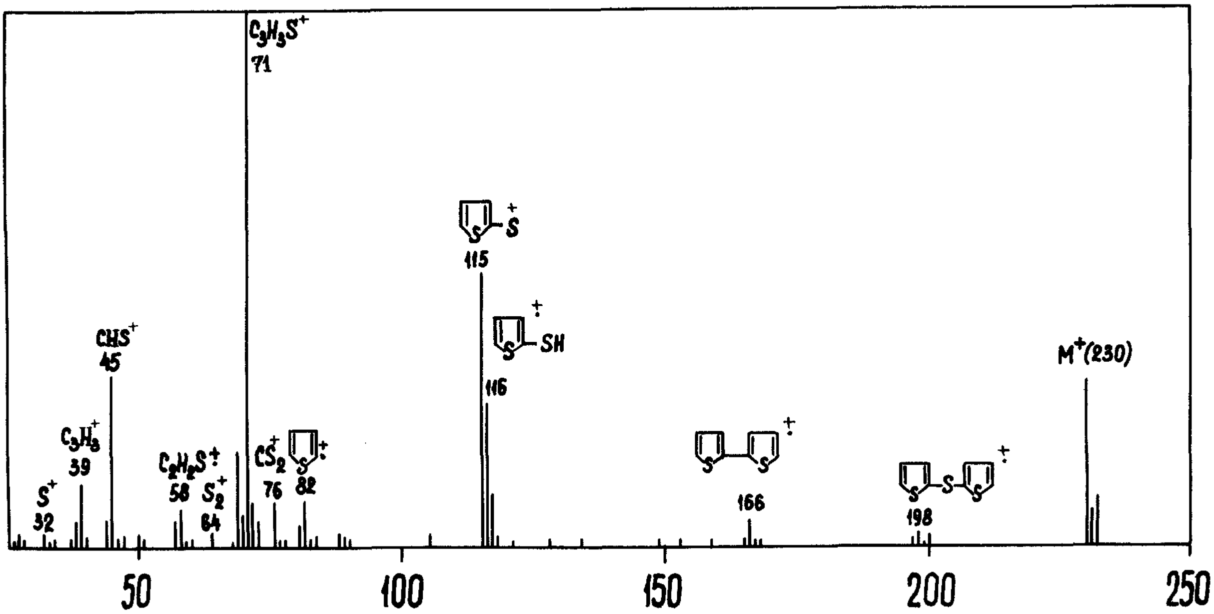


FIGURE 2 The mass spectrum of 2,2′-dithienyldisulfide. Mass spectrometer MH-1303 (USSR), ionization energy 50 eV, temperature of admission system 30°C, direct admission. The metastable peaks *m*/*e* 120 (23 → 166); 57.5 (230 → 115); 43.8 (115 → 71).

TABLE I

Atomic coordinates and temperature factors

Atom	x	y	z	B_j, Å^2
S(1)	0.3197(7)	0.2500	−0.3172(6)	4.2(2)
S(2)	0.3137(5)	0.0987(3)	−0.3912(5)	4.9(1)
S(3)	0.4844(5)	0.0750(2)	−0.3095(5)	4.6(1)
S(4)	0.3589(5)	0.0372(3)	−0.0726(4)	4.2(1)
S(5)	0.2959(6)	0.0729(3)	0.1889(5)	4.9(1)
S(6)	0.1135(5)	0.0993(3)	0.1428(5)	4.7(1)
S(7)	0.1075(7)	0.2500	0.2135(6)	4.3(2)
C(1)	0.3239(17)	0.1831(9)	−0.4230(15)	3.9(4)
C(2)	0.3183(18)	0.2130(9)	−0.5394(16)	4.2(4)
C(3)	0.4495(20)	0.0918(9)	−0.1573(18)	5.1(4)
C(4)	0.4949(20)	0.1456(10)	−0.0907(18)	5.8(5)
C(5)	0.4495(20)	0.1448(10)	0.0293(18)	5.7(5)
C(6)	0.3771(16)	0.0894(8)	0.0516(15)	3.6(4)
C(7)	0.1222(16)	0.1844(9)	0.1041(15)	3.8(4)
C(8)	0.1539(18)	0.2121(9)	−0.0069(15)	4.2(4)

significant since this peak is absent in the mass spectrum of 2,2′-dithienyldisulfide. In other words, the mass spectra confirm that in the presence of crown ether the polymer, which differs from cyclic tetramer, is formed. One can assume that this polymer contains a linear combination of fragments (**8**).

5. x-Ray study.

The distinction between linear and cyclic polysulfides consists of the amorphous structure of the former and the crystalline structure of the latter.

A sample of the cyclic tetramer (**3**) was prepared by a crystallization from chloroform–toluene mixture, which produced two crystal types: rhombic plates and needles. The plates were twinned and were subjected only to a preliminary study. They are monoclinic with $a = 11.78$, $b = 10.72$, $c = 9.78$ Å, $\beta = 109.0°$, $D_m = 1.63$ g. cm^{-3}, $D_c = 1.69$ g. cm^{-3}, $Z = 2$, space group $P2_1/c$, $P2/c$ or Pc.

The needle-shaped crystals are orthorhombic with $a = 10.642(3)$, $b = 19.409(4)$, $c = 11.074(3)$ Å, $D_c = 1.71$ g. cm^{-3}, $Z = 4$, space group $Pnma$ (by systematic extinction and intensity statistics). Intensities were measured with an automatic four-circle "Hilger & Watts" diffractometer (Cu-radiation, graphite monochromator, ω-scan within $\theta \leqslant 50°$, no absorption correction). The total number of reflections with $F^2 > 3\sigma$ is 688. Determination of unit cell parameters, intensity measurement and structure factor calculation were performed according to Ref. 7.

All subsequent calculations were carried out with programs written by V. I. Andrianov, B. L. Tarnopol'skii and Z. Sh. Safina. The structure was solved by the direct method of Sayre-Zahariassen-Cochran implemented in the program.[8] E-Synthesis with the best sign variant permitted location of 7 sulfur atoms (2 of which were in a special position in an m plane) and 6 carbons. A subsequent electron density synthesis ($R = 0.257$) revealed two missing carbon atoms. The structure was refined by an isotropic least-squares technique with Cruickshank weights to $R = 0.104$. Atomic coordinates and temperature factors are given in Table I.

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