Chemistry of Heterocyclic Compounds, Vol. 34, No. 6, 1998

SYNTHESIS OF HETEROCYCLES FROM THE PRODUCTS OF THE ADDITION OF POLYHALOALKANES TO UNSATURATED SYSTEMS.

8*. SYNTHESIS OF SEVERAL THIAZOLE DERIVATIVES FROM 3-THIOCYANATO-5,5,5-TRICHLORO-2- PENTANONE. THEIR MOLECULAR AND CRYSTAL STRUCTURE

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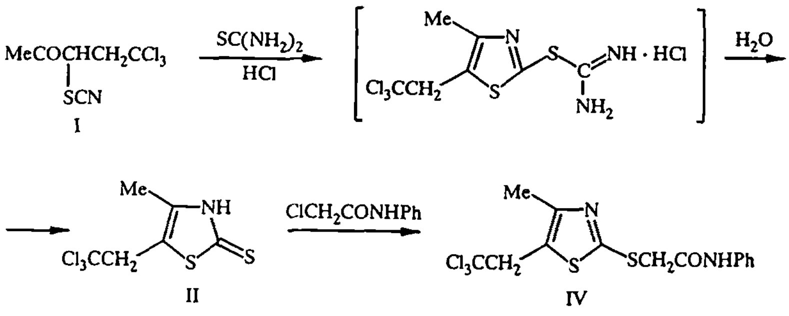
4-Methyl-5-(2,2,2-trichloroethyl) derivatives of 2-thiazolethione and 2-amino-3-hydroxythiazolium chloride were synthesized from 3-thiocyanato-5,5,5-trichloro-2-pentanone. The structures of these derivatives were determined using spectral data and x-ray diffraction structural analysis.

In previous work [2], we demonstrated the feasibility of synthesizing substituted thiazoles from the product of the homolytic addition of CCl_4 to methyl vinyl ketone, namely, 3,5,5,5-tetrachloro-2-pentanone, as well as 3-thiocyanato-5,5,5-trichloro-2-pentanone (I), which is readily obtained from replacement of the α-chlorine atom by an SCN group. In particular, the corresponding 4-methyl-5-(2,2,2-trichloroethyl) derivatives of 2-phenylaminothiazole, 2-thiazolone, and 2-chlorothiazole were synthesized by the Chernyak method from thiocyanatoketone I under mild conditions in good yield [3]. In the present work, 4,5-disubstituted thione II and 2-amino-3-hydroxythiazolium chloride III were synthesized from thiacyanatoketone I. Furthermore, thione II was converted through the corresponding anion to thiol derivative IV using the method proposed for similar compounds by Shestopalov [4].

The reaction of thiocyanatoketone I with thiourea in the presence of hydrochloric acid was used to obtain thione II. A similar transformation described by Gregory [5] and Vernin [6] probably occurs through the corresponding isothiuronium salt [3]. Thione II, which may be capable of tautomerization, exists exclusively in thione form. Thus, the ^1H and ^{13}C NMR spectra of this compound in DMSO-d_6 are in good accord with the data for a model compound, 5-methylthiazole-2(3H)-thione [7]. The IR spectra taken for KBr pellets displays bands at 1480, 1260, 1080, and 895 cm^{-1}, corresponding to the C=S group of thiazole-2-thiones [8].



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*For Communication 7, see [1].

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TABLE 1. Bond Angles ω in II

Bond angle	ω, deg	Bond angle	ω, deg
$C_{(2)}—S_{(1)}—C_{(5)}$	92,4(1)	$S_{(1)}—C_{(5)}—C_{(6)}$	121,6(2)
$C_{(2)}—N_{(3)}—C_{(4)}$	116,8(2)	$C_{(4)}—C_{(5)}—C_{(6)}$	127,9(3)
$S_{(1)}—C_{(2)}—S_{(2)}$	125,0(2)	$C_{(5)}—C_{(6)}—C_{(7)}$	115,8(3)
$S_{(1)}—C_{(2)}—N_{(3)}$	108,3(2)	$Cl_{(1)}—C_{(7)}—Cl_{(2)}$	109,3(2)
$S_{(2)}—C_{(2)}—N_{(3)}$	126,7(2)	$Cl_{(1)}—C_{(7)}—Cl_{(3)}$	109,1(2)
$N_{(3)}—C_{(4)}—C_{(5)}$	112,2(2)	$Cl_{(2)}—C_{(7)}—Cl_{(3)}$	107,6(2)
$N_{(3)}—C_{(4)}—C_{(8)}$	118,6(3)	$Cl_{(1)}—C_{(7)}—C_{(6)}$	108,3(2)
$C_{(5)}—C_{(4)}—C_{(8)}$	129,2(3)	$Cl_{(2)}—C_{(7)}—C_{(6)}$	111,4(2)
$S_{(1)}—C_{(5)}—C_{(4)}$	110,3(2)	$Cl_{(3)}—C_{(7)}—C_{(6)}$	111,2(2)

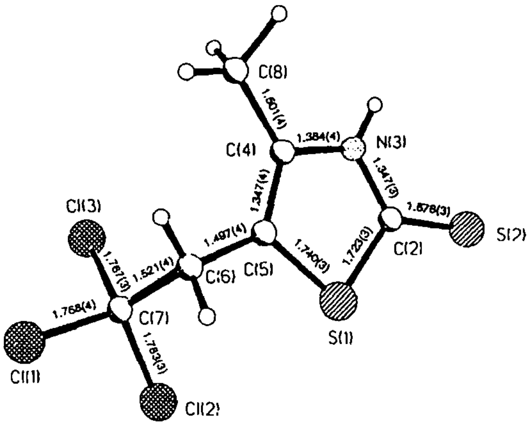


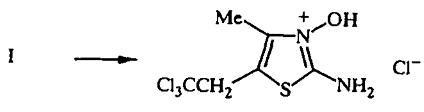
Fig. 1. General view of II with bond lengths.

The structure of II was also studied by x-ray diffraction. Figure 1 shows a general view of this molecule and the bond lengths. The bond angles are given in Table 1. The x-ray diffraction data indicate a thione structure and the length of the exocyclic C=S bond is almost the same as the value reported for 4-substituted thiazole-2-thiones [9, 10] and rigid 3-alkylthiazole-2-thiones [11]. The planar structure of the heterocycle (to ±0.001 Å) provides for conjugation between its fragments as indicated by the levelling of the bond lengths in the ring, which are similar to the values found for thiazole [12] and substituted thiazoles [13, 14], and to the standard lengths of the corresponding bonds [15].

The intermolecular hydrogen bonds $N_{(3)}-H_{(3)}\cdots S_{(2)}$ $(-x - 1, 1 - y, -z)$ [$N_{(3)}\cdots S_2$, 3.31(3); $N_{(3)}-H_{(3)}$, 0.86(3), $H_{(3)}\cdots S_{(2)}$, 2.46(3) Å; $N_{(3)}-H_{(3)}\cdots S_2$, 171(2)°] connect molecules of II into centrosymmetric dimers (Fig. 2). Analysis of the molecular packing showed an intermolecular nonbonding contact $Cl_{(3)}\cdots S_{(1)}$ $(x, 1.5 - y, z - 0.5)$ 3.500 Å, which is comparable to the sum of the van der Waals radii of the chlorine and sulfur atoms (3.53 Å [16]).

α-Thiocyanatoketones react with hydroxylamine to give 2-aminothiazole 3-oxides or the hydrochloride salts, 2-amino-3-hydroxythiazolium chlorides [17]. We used this method to obtain III from ketone I.

In light of the virtual lack of experimental data, which would permit us to consider the localization of charge in cations such as III, we studied the ^{13}C NMR spectra of salt III and carried an x-ray diffraction structural study of this salt, which is the first such investigation of an O-protonated thiazole N-oxide. The IR and PMR spectra of this salt were also taken. The PMR spectra were found to be in accord with the corresponding spectra of related compounds [18, 19]. A strong band is found in the IR spectrum of salt III at 1620 cm^{-1}, related to the C=N bond, as well as broad bands at 2500-330 cm^{-1} related to stretching vibrations of N−H and O−H bonds.



III

TABLE 2. Bond Angles ω in the Cation of Salt III

Bond angle	ω, deg	Bond angle	ω, deg
$C_{(2)}—S_{(1)}—C_{(5)}$	90,8(1)	$S_{(1)}—C_{(5)}—C_{(4)}$	111,5(2)
$O_{(1)}—N_{(3)}—C_{(2)}$	119,9(2)	$S_{(1)}—C_{(5)}—C_{(6)}$	120,4(2)
$O_{(1)}—N_{(3)}—C_{(4)}$	122,5(2)	$C_{(4)}—C_{(5)}—C_{(6)}$	128,0(2)
$C_{(2)}—N_{(3)}—C_{(4)}$	117,3(2)	$C_{(5)}—C_{(6)}—C_{(7)}$	115,7(2)
$S_{(1)}—C_{(2)}—N_{(3)}$	109,5(1)	$Cl_{(1)}—C_{(7)}—Cl_{(2)}$	109,1(1)
$S_{(1)}—C_{(2)}—N_{(9)}$	126,7(2)	$Cl_{(1)}—C_{(7)}—Cl_{(3)}$	108,7(1)
$N_{(3)}$—C(2)—$N_{(9)}$	123,8(2)	$Cl_{(2)}—C_{(7)}—Cl_{(3)}$	107,7(1)
$N_{(3)}—C_{(4)}—C_{(5)}$	110,9(2)	$Cl_{(1)}—C_{(7)}—C_{(6)}$	108,2(2)
$N_{(3)}—C_{(4)}—C_{(8)}$	118,6(2)	$Cl_{(2)}—C_{(7)}—C_{(6)}$	111,3(1)
$C_{(5)}—C_{(4)}—C_{(8)}$	130,5(2)	$Cl_{(3)}—C_{(7)}—C_{(6)}$	112,0(1)

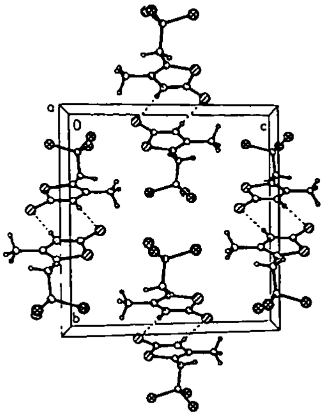


Fig. 2. Projection *bc* of the crystal structure of II (the intermolecular N−H···S hydrogen bond are shown by dotted lines).

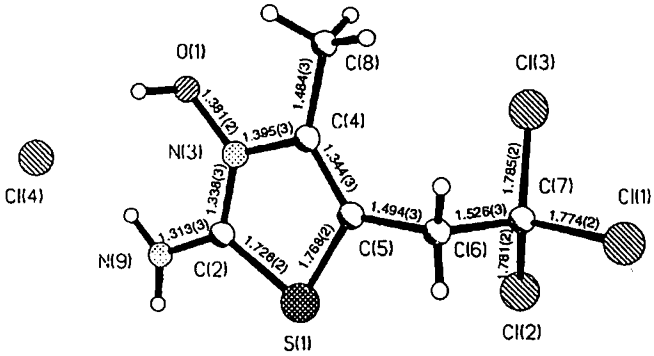


Fig. 3. General view of salt III with bond lengths in the cation.

Since there have been no x-ray diffraction structural data for 2-amino-3-hydroxythiazolium salts, salt III will be compared with 2-aminothiazolium salts, possessing a hydrogen atom at $N_{(3)}$ as well as neutral aminothiazole, 2-thiazolimine, 2-thiazolone, and 2-thiazolethione derivatives. A general view of salt III derived from the x-ray diffraction data with bond lengths in the cation is shown in Fig. 3, while the bond angles are given in Table 2.

All the atoms of the heterocycle in cation III are found in a single plane (with deviations of ±0.003 Å), which is favorable for conjugation. The $C_{(2)}-N_{(3)}$, $C_{(2)}-N_{(9)}$, and $C_{(2)}-S_{(1)}$ bond lengths suggest that the positive charge is delocalized over the atoms of these bonds, which may be described using cation resonance forms IIIa-IIIc.

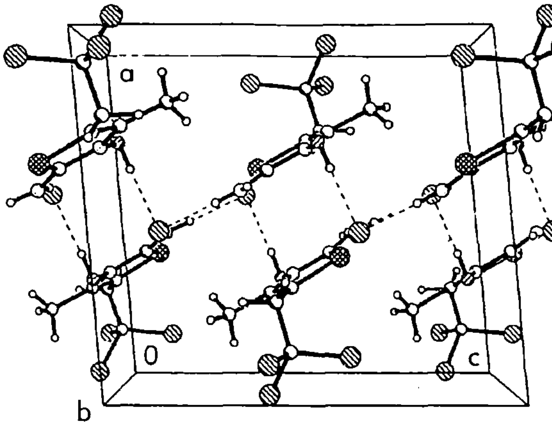
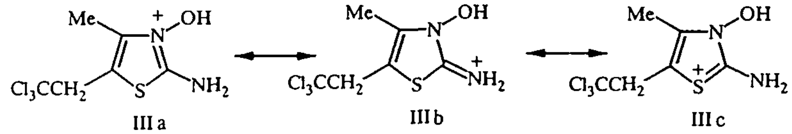


Fig. 4. Projection *ac* of the crystal structure of III. The intermolecular O−H···Cl and N−H···Cl hydrogen bonds are shown by dashed lines.



The exocyclic $C_{(2)}-N_{(9)}$ bond (1.313(3) Å) in cation III is similar in length to the corresponding bond in 2-aminothiazolium trichloroacetate [20] and markedly shorter than not only the C−N bonds in 2-aminothiazoles but also the C=N double bond in 2-phenylsulfonylimino-3-thiazoline [21], which may be attributed to the contribution of resonance form IIIb. The $C_{(2)}-S_{(1)}$ bond length in cation III (1.726(2) Å) is virtually the same as the corresponding bond length in 2-aminothiazolium trichloroacetate and less than the corresponding values in the abovementioned imine or thione II as well as in various thiazoles [12-15], which may be seen as a result of the contribution of resonance form IIIc. We should note that the $C_{(5)}-S_{(1)}$ bond length (1.768(2) Å) is much greater than the values for this bond in various thiazoles [12-15] and thiazole salts [13, 20-24]. This discrepancy may be attributed to a diminished transmission of conjugation through this bond.

The cations and anions in the crystal of salt III are connected in a three-dimensional framework (Fig. 4) by hydrogen bonds: $O_{(1)}-H_{(10)}\cdots Cl_{(4)}$ (1 − *x*, 2 − *y*, 1 − *z*) [$O_{(1)}\cdots Cl_{(4)}$, 2.951(2); $O_{(1)}-H_{(10)}$, 0.88(2); $H_{(10)}\cdots Cl_{(4)}$, 2.07(2) Å; $O_{(1)}-H_{(10)}\cdots Cl_{(4)}$, 178(2)°], $N_{(9)}-H_{(91)}\cdots Cl_{(4)}$ (1 − *x*, *y* − 0.5, 0.5 − *z*) [$N_{(9)}\cdots Cl_{(4)}$, 3.117(2); $N_{(9)}-H_{(91)}$, 0.86(2); $H_{(91)}\cdots Cl_{(4)}$, 2.28(2) Å; $N_{(9)}-H_{(91)}\cdots Cl_{(4)}$, 165(2)°], $N_{(9)}-H_{(92)}\cdots Cl_{(4)}$ (*x*, *y*, *z*) [$N_{(9)}\cdots Cl_{(4)}$, 3.252(2); $N_{(9)}-H_{(92)}$, 0.88(2); $H_{(92)}\cdots Cl_{(4)}$, 2.43(2) Å; $N_{(9)}-H_{(92)}\cdots Cl_{(4)}$, 156(2)°].

EXPERIMENTAL

The ^1H NMR spectra were taken on a Bruker AM-300 spectrometer at 300 MHz and the ^{13}C NMR spectra were taken on a Bruker AC-200 spectrometer at 50 MHz. The IR spectra for KBr pellets were taken on a Perkin−Elmer 577 spectrometer.

3-Thiocyanato-5,5,5-trichloro-2-pentanone (I) was obtained according to our previous procedure [2].

4-Methyl-5-(2,2,2-trichloroethyl)thiazole-2(3H)-thione (II). A solution of 6.76 g (0.03 mole) ketone I and 4.57 g (0.06 mole) thiourea in a mixture of 60 ml water, 24 ml ethanol, and 15 ml conc. hydrochloric acid was heated at reflux for 8-10 h and cooled. Then, 10-15 ml cold water was added. The precipitate formed was filtered off, washed with a small amount of aqueous ethanol, and dried to give 6.27 g (87%) thione II, mp 211.5-213.0°C (from aqueous ethanol, dec.). PMR spectrum in DMSO-d_6: 13.20 (H, s, NH), 4.10 (2H, s, CH_2), 2.20 ppm (3H, s, CH_3). ^{13}C NMR spectrum in DMSO-d_6: 187.4 (CS), 139.6 ($C_{(4)}$), 114.7 ($C_{(5)}$), 98.8 (CCl_3), 49.8 (CH_2), 12.1 ppm (CH_3). Found: C, 27.62; H, 2.35; Cl, 40.53; N, 5.31; S, 24.44%. Calculated for $C_6H_6Cl_3NS_2$: C, 27.44; H, 2.30; Cl, 40.50; N, 5.33; S, 24.42%.

4-Methyl-5-(2,2,2-trichloroethyl)-2-(phenylaminocarbonylmethylthio)thiazole (IV). Solutions of 0.29 g KOH in 2.5 ml water and of 0.85 g (5 mmoles) chloroacetic acid anilide in 3 ml DMF consecutively were slowly added dropwise to a solution of 1.32 g (5 mmoles) thione II in 10 ml DMF with stirring at ~20°C. The reaction mixture was then heated with

TABLE 3. Atomic Coordinates (×10^4, ×10^3 for H) in II

Atom	x	y	z
$Cl_{(1)}$	4947(2)	8660(1)	-757(1)
$Cl_{(2)}$	3018(2)	8684(1)	1101(1)
$Cl_{(3)}$	573(2)	8978(1)	-1040(1)
$S_{(1)}$	310(1)	6498(1)	1199(1)
$S_{(2)}$	-3502(1)	5475(1)	1667(1)
$N_{(3)}$	-2573(4)	5890(2)	-282(2)
$C_{(2)}$	-2071(4)	5915(2)	811(2)
$C_{(4)}$	-1160(4)	6313(2)	-826(2)
$C_{(5)}$	524(4)	6684(2)	-140(2)
$C_{(6)}$	2441(5)	7122(2)	-415(3)
$C_{(7)}$	2721(5)	8299(2)	-284(3)
$C_{(8)}$	-1665(6)	6311(3)	-2045(3)
$H_{(3)}$	-368(5)	557(3)	-59(3)
$H_{(61)}$	377(5)	680(2)	2(2)
$H_{(62)}$	238(5)	699(3)	-116(3)
$H_{(81)}$	-273(8)	564(4)	-237(4)
$H_{(82)}$	-42(7)	645(4)	-241(3)
$H_{(83)}$	-286(9)	677(4)	-235(4)

TABLE 4. Atomic Coordinates (×10^4, ×10^3 for H) in Salt III

Atom	x	y	z
$Cl_{(1)}$	9024(1)	757(1)	6040(1)
$Cl_{(2)}$	8947(1)	2498(1)	4019(1)
$Cl_{(3)}$	10069(1)	3611(1)	6146(1)
$Cl_{(4)}$	5532(1)	11014(1)	3578(1)
$S_{(1)}$	6274(1)	4779(1)	4035(1)
$O_{(1)}$	6980(2)	8287(2)	5638(2)
$N_{(3)}$	6804(2)	6886(2)	5301(2)
$N_{(9)}$	5612(2)	7548(2)	3619(2)
$C_{(2)}$	6192(2)	6587(2)	4288(2)
$C_{(4)}$	7341(2)	5745(2)	5934(2)
$C_{(5)}$	7144(2)	4511(2)	5368(2)
$C_{(6)}$	7496(2)	3040(2)	5768(2)
$C_{(7)}$	8812(2)	2515(2)	5505(2)
$C_{(8)}$	7993(2)	6035(3)	7076(2)
$H_{(10)}$	623(3)	851(3)	586(2)
$H_{(61)}$	750(2)	300(2)	660(2)
$H_{(62)}$	692(2)	238(3)	549(2)
$H_{(81)}$	883(2)	636(3)	702(2)
$H_{(82)}$	751(3)	673(4)	748(3)
$H_{(83)}$	810(3)	521(4)	754(3)
$H_{(91)}$	527(3)	729(3)	296(2)
$H_{(92)}$	570(3)	845(3)	382(2)

stirring on a steam bath for 0.5-1 h and cooled. A small amount of cold water was added. The precipitate formed was filtered off and recrystallized from aqueous ethanol to give 1.53 g (77%) sulfide IV, mp 139.0-140.4°C (from aqueous ethanol). PMR Spectrum in DMSO-d_6: 10.25 (1H, br. s, NH), 7.57 (2H, d, *o*-H, J = 8 Hz), 7.31 (2H, t, *m*-H, J = 8 Hz), 7.07 (1H, t, *p*-H, J = 8 Hz), 4.27 (2H, s, CH_2), 4.19 (2H, s, CH_2), 2.37 ppm (3H, s, CH_3). ^{13}C NMR Spectrum in DMSO-d_6: 165.3 ($C_{(2)}$), 162.3 (CO), 152.7 ($C_{(4)}$), 138.6 (*ipso*-C), 128.7 (*m*-C), 123.5 (*p*-C), 122.6 ($C_{(5)}$), 119.1 (*o*-C), 99.1 (CCl_3), 50.1 (CH_2CCl_3), 38.1 (SCH_2), 15.6 ppm (CH_3). Found: C, 42.68; H, 3.44; Cl, 26.64; N, 7.08; S, 16.05%. Calculated for $C_{14}H_{13}Cl_3N_2OS_2$: C, 42.49; H, 3.31; Cl, 26.88; N, 7.08; S, 16.20%.

2-Amino-3-hydroxy-4-methyl-5-(2,2,2-trichloroethyl)thiazolium Chloride (III). A mixture of 2.47 g (0.01 mole) thiocyanatoketone I and 0.7 g (0.01 mole) hydroxylamine hydrochloride in 5 ml ethanol was heated at reflux until completely homogeneous (72 h) and then maintained at ~20°C for 24 h. The precipitate formed was filtered off and washed with ethanol to give 2.14 g (75.5%) salt III, mp 215°C (dec.). PMR Spectrum in DMSO-d_6: 13.25 (1H, sh, OH), 9.78 (2H, br.s, NH_2), 4.28 (2H, s, CH_2), 2.30 ppm (3H, s, CH_3). ^{13}C NMR Spectrum in DMSO-d_6: 161.7 ($C_{(2)}$), 137.6 ($C_{(4)}$), 104.4 ($C_{(5)}$), 98.6 (CCl_3), 49.4 (CH_2), 11.6 ppm (CH_3). Found: C, 24.47; H, 2.70; Cl, 47.11; N, 9.96; S, 10.84%. Calculated for $C_6H_8Cl_4N_2OS$: 24.18; H, 2.71; Cl, 47.58; N, 9.40; S, 10.76%.

X-Ray Diffraction Structural Study of II and III. The unit cell parameters of monoclinic crystals of II at 20°C: $a = 6.640(2)$, $b = 12.782(3)$, $c = 12.603(4)$ Å, $\beta = 102.22(2)°$, $V = 1045(1)$ Å^3, $d_{calc} = 1.662$ g/cm^3, space group $P2_1/c$, $Z = 4$. The unit cell parameters of monoclinic crystals of III at -125°C: $a = 10.496(2)$, $b = 9.379(2)$, $c = 11.860(2)$ Å, $\beta = 95.38(2)°$, $V = 1162.4(7)$ Å^3, $d_{calc} = 1.703$ g/cm^3, space group $P2_1/c$, $Z = 4$. The unit cell parameters and intensities of 2866 independent reflections for II and 2370 independent reflections for III were measured on a Siemens P3/PC automatic four-circle diffractometer using λMoK_α radiation, graphite monochromator, and $\theta/2\theta$ scanning to θ_{max} 28 (II) and 27° (III). The structures were solved by the direct method, revealing all the nonhydrogen atoms, and refined anisotropically by the method of least squares using 2007 reflections with $I > 3\sigma(I)$ for II and 1874 reflections with $I > 2\sigma(I)$ for III. All the hydrogen atoms were found in the difference maps and refined isotropically. The final discrepancy factors $R = 0.041$, $R_w = 0.041$ for II and $R = 0.025$, $R_w = 0.025$ for III. All the calculations were carried out using the SHELXTL program (PC version) [23]. The atomic coordinates are given in Tables 3 and 4. The temperature parameters may be obtained from the authors.

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