

New reaction of the sodium salt of 2-nitroethanol. X-ray analysis of the sodium salt of 2-oxo-3-hydroxypropionic acid oxime, 2-bromo-2-nitropropane-1,3-diol, and the model 2,2-dinitropropane-1,3-diol

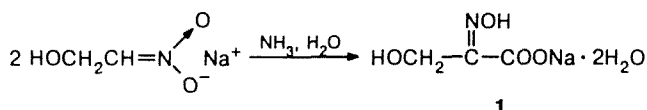
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A novel reaction of the sodium salt of 2-nitroethanol in aqueous ammonia resulted in the sodium salt of 2-oxo-3-hydroxypropionic acid oxime (**1**) has been found. Bromination of **1** affords 2-bromo-2-nitropropane-1,3-diol (**2**) with a previously unknown molecular conformation. The formation mechanisms of compounds **1** and **2** were suggested. X-ray analysis of products **1**, **2** and that of the model compound, 2,2-dinitropropane-1,3-diol, was performed.

Key words: 2-nitroethanol, sodium salt; 2-oxo-3-hydroxypropionic acid oxime, sodium salt; 2-bromo-2-nitropropane-1,3-diol, 2,2-dinitropropane-1,3-diol, synthesis, X-ray analysis; molecular structure, stereochemistry.

We found a previously unknown transformation of the sodium salt of 2-nitroethanol into the sodium salt of oxime of 2-oxo-3-hydroxypropionic acid (**1**) (81.5 % yield) in aqueous ammonia at ~50 °C.



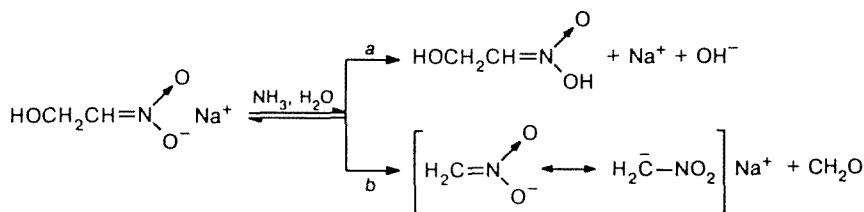
Compound **1** is fairly stable (m.p. 109–110 °C, decomp.); according to the elemental analysis data its molecule contains 2 moles of crystallization water. It should be noted that, firstly, urotropin is obtained along with product **1**, and, secondly, compound **1** is not produced in the absence of NH₃. It is easy to assume that nitroethanol as the product of the reaction between nitromethane and formaldehyde^{1,2} dissociates in the alkaline medium with the formation both of aci-form of 2-nitroethanol and the nitromethane anion (Scheme 1); the electron structure of

the latter can be represented by two resonance structures.

In this case the liberating formaldehyde reacts with ammonia to give urotropin and to shift the equilibrium to the right. Thus, NH₃ favors the generation of aci-form of 2-nitroethanol (direction *a*) and mesomeric anion of nitromethane (direction *b*). In this connection, one can suggest the following mechanism of the formation of product **1** (Scheme 2). Obviously, the success of the reaction is mostly determined by participation of the nitromethane carbanion therein.

According to the X-ray analysis data, salt **1** is an ionic compound and crystallizes in space group *P* $\bar{1}$. The conformation of anion **1** (Fig. 1) and the bond lengths (Table 1) are evidence for the charge delocalization over the planar fragment of the anion, where O(1), O(2), C(1), C(2), C(3), and N(1) atoms lie nearly in the same plane. Torsion angles O(1)–C(1)–C(2)–C(3), O(1)–C(1)–C(2)–N(1), O(2)–C(1)–C(2)–C(3), and O(2)–C(1)–C(2)–N(1) are 5.3°, 176.2°, 176.2°, and 2.3°, respectively, while torsion angles

Scheme 1



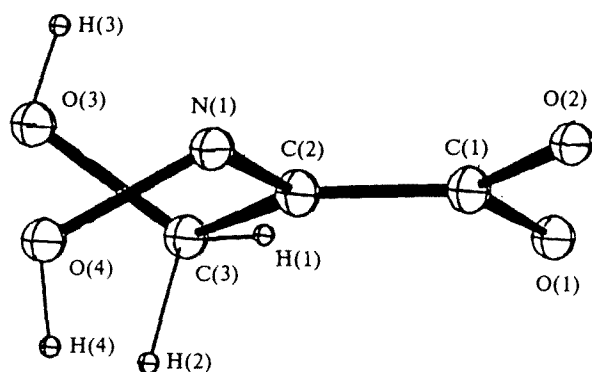
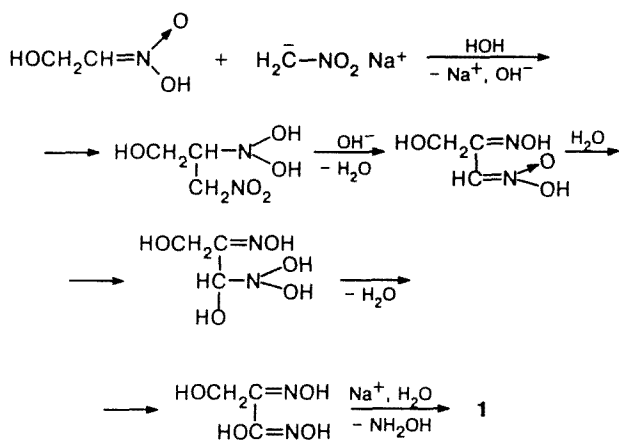


Fig. 1. The conformation of anion 1.

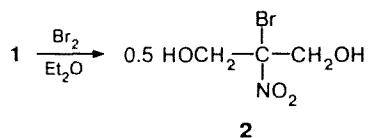
Scheme 2



O(3)—C(3)—C(2)—N(1) and O(3)—C(3)—C(2)—C(1) amount to 40.5° and 137.9°, respectively.

We failed to isolate 2-oxo-3-hydroxypropionic acid oxime by treatment of compound 1 with aqueous solutions of mineral acids; in this case, decomposition of mixtures accompanied by heat release, gas evolution and blue coloring was observed.

Bromination of compound 1 in ether at 0 °C leads to 2-bromo-2-nitropropane-1,3-diol (2) in 89 % yield.

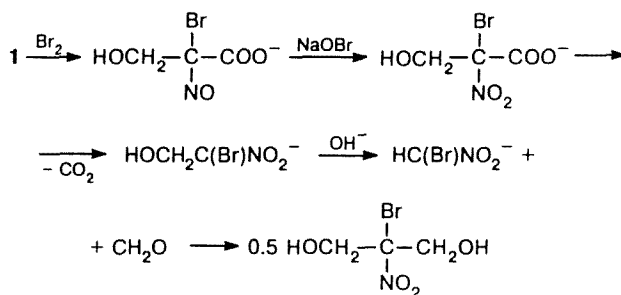


This result can be explained by successive reactions of bromination to a bromonitroso derivative, its oxidation to a bromonitro derivative (cf. Ref. 3), decarboxylation and disproportionation of 2-bromo-2-nitroethanol *via* dissociation with CH₂O liberation and subsequent hydroxymethylation (Scheme 3).

Table 1. The bond lengths (*d*) in the anion of salt 1

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
C(1)—C(2)	1.293	O(4)—H(4)	0.865
C(2)—C(3)	1.513	C(3)—O(3)	1.435
C(1)—O(1)	1.328	O(3)—H(3)	0.909
C(1)—O(2)	1.333	C(3)—H(1)	0.998
C(2)—N(1)	1.515	C(3)—H(2)	0.991
N(1)—O(4)	1.437	O(4)—H(4)	0.865

Scheme 3



To identify product 2 by means of an alternative synthesis (by bromination of the sodium salt of 2-nitropropane-1,3-diol⁴) the sample 2a was obtained. The molecular and crystal structures of compound 2a are known.⁵ We carried out an X-ray investigation of crystals 2 and 2a (repeatedly); the results obtained for compound 2a coincided with literature data.⁵

A comparison between geometric parameters of crystals 2 (which were separated after bromination of compound 1 followed by incomplete ether distillation *in vacuo* without special crystallization from organic solvents) and those of crystals 2a showed that both crystals represented different phases. Synthesized from different starting compounds, crystals of 2 and 2a have the same space group *Cc* but differ in their unit cell parameters and density, the observed differences lying beyond the limits of measurement accuracy.

The molecular packing in structures 2 and 2a is almost the same except that of terminal OH groups. One can see from Figs. 2 and 3 that molecules 2 and 2a possess different conformations. The O—O and C—C bonds in molecule 2 are in the synclinal position, while in molecule 2a they are antiperiplanar. The Newman projections for molecules 2 and 2a are shown in Scheme 4.

The indicated differences manifest themselves in the values of the torsion angles: O(1)—C(1)—C(2)—C(3) and O(2)—C(3)—C(2)—C(1) in molecule 2 are 48.2° and 54.6°, respectively, while in molecule 2a torsion angles O(1)—C(3)—C(1)—C(2) and O(2)—C(2)—C(1)—C(3) are 174.5° and 167.5°, respectively.

As follows from the experimental data, the conformation of molecule 2 can be considered as being built in the conformation of the fragment $\text{>C}-\text{CH}_2\text{OH}$ of the anion 1

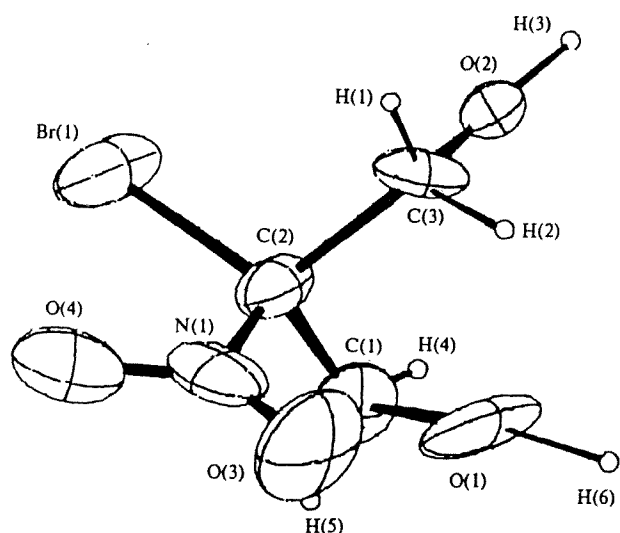


Fig. 2. The structure of molecule 2.

and is conserved until the moment of isolation of the molecule 2. In their turn, the conformational differences in positions of the OH groups in molecules 2 and 2a create different architectures of the H-bonds in the crystals of these conformers. The distance between the oxygen atoms of neighboring molecules O(1)...O(2) is 3.044 Å in the structure 2, while the same distances in the structure 2a are 2.712 Å. In both cases the H-bonds form indefinite chains: in structure 2 the chain is generated by *c* plane, in structure 2a — by *n* plane. The calculations of energy for two structures by the atom-atom potential method con-

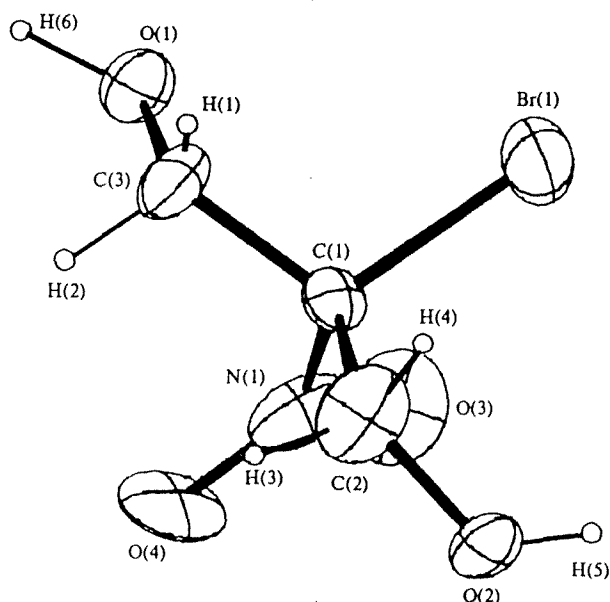
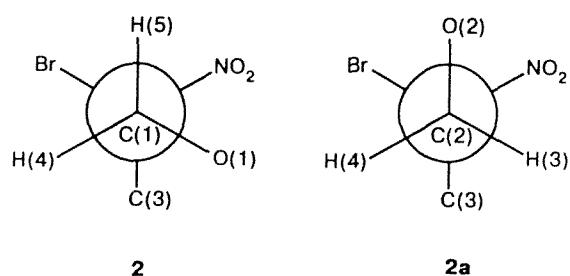


Fig. 3. The structure of molecule 2a.

Scheme 4



sidering the H-bond energy show that the crystal structure 2a is 4.24 kcal mol⁻¹ more favorable energetically than that of 2 including the contribution of H-bonds (1.66 kcal mol⁻¹). According to SCF MO/STO-3G calculations, the overall electron energy of both molecules 2 and 2a is essentially the same; calculations of the strain energy for two conformers give different values. The conformation of molecule 2 is more favorable in comparison with that of 2a by 1.5 kcal mol⁻¹. Thus, the unfavorable conformation of 2a is compensated by a gain in the energy of H-bonds in crystal.

We observed for 2,2-dinitropropane-1,3-diol (3) the synclinal position of C—O and C—C bonds similar to that for diol 2 (Fig. 4). This is explained by the influence of bulky substituents in position 2 (*gem*-dinitro group). In molecule 3 torsion angles O(1)—C(1)—C(2)—C(3) and O(2)—C(3)—C(2)—C(1) are 64.3° and 56.8°, respectively, while terminal OH groups form two indefinite chains with short distances between the oxygen atoms: O(1)...O(2)

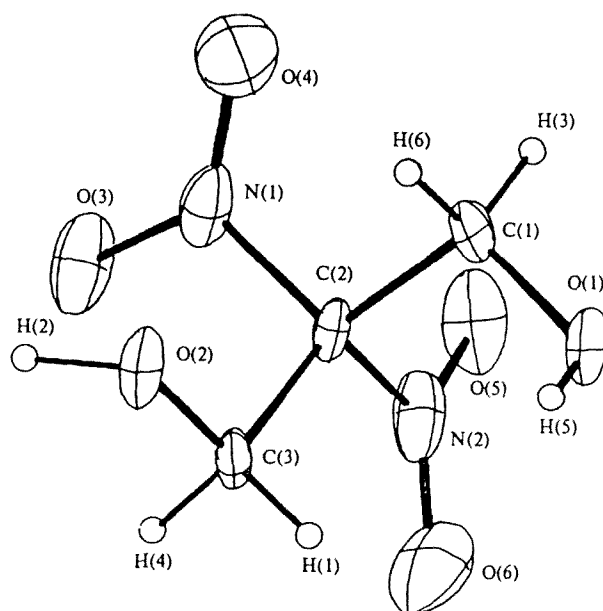


Fig. 4. The structure of molecule 3.

(2.651 Å) and O(1)...O(2) (2.700 Å).

A comparison of the results obtained with the literature data⁶⁻⁸ shows that conformational variety is characteristic of the molecules of $\text{RC}(\text{CH}_2\text{OH})_3$ and $\text{R}_2\text{C}(\text{CH}_2\text{OH})_2$ type.

Experimental

Sodium salt of 2-oxo-3-hydroxypropionic acid oxime (1). A solution of sodium salt of 2-nitroethanol (10.72 g, 95 mmol) in water (12 mL) and 25 % aqueous NH_3 (5.4 mL, 95 mmol) was stirred for 1 h at 48–52 °C. The reaction mixture was cooled to ~20 °C and diluted with 20 mL of an ethanol–ether (1 : 1) mixture; the precipitate was filtered off and washed with 20 mL of the ethanol–ether (1 : 1) mixture. A light-beige precipitate of salt **1** (4.44 g) was obtained, m.p. 107–109 °C. The filtrate was combined with the wash mixture and allowed to stay in the refrigerator for 48 h; precipitated crystals were filtered off. An additional amount of **1** (2.4 g) was obtained, m.p. 107–109 °C. The total yield was 6.84 g (81.5 %). After reprecipitation of the salt **1** from a water–methanol solution by ether, crystals with m.p. 109–110 °C were obtained. Found (%): C, 20.2; H, 4.4; N, 8.0. $\text{C}_3\text{H}_8\text{NNaO}_6$. Calculated (%): C, 20.34; H, 4.52; N, 7.91.

The crystals of **1** for X-ray analysis were selected from the total salt mass obtained after reprecipitation.

2-Bromo-2-nitropropane-1,3-diol (2). To a suspension of sodium salt **1** (0.7 g, 4 mmol) in ether (50 mL) at 0 °C, bromine (0.38 mL, 7 mmol) was added under stirring, and stirring was continued for 30 min at 0 °C. The NaBr precipitate was filtered off and washed with ether; combined ether solutions were concentrated to a quarter of their volume; several crystals of **2** (m.p. 115–117 °C) were taken for an X-ray analysis. The ether was evaporated to dryness, a pale-yellow crystalline residue was obtained. After twice crystallization from dichloroethane compound **2** (0.395 g, 88.6 %) was obtained as white needles, m.p. 125–127 °C. Found (%): C, 17.8; H, 3.2; N, 6.8; Br, 39.8. $\text{C}_3\text{H}_6\text{BrNO}_4$. Calculated (%): C, 18.0; H, 3.00; N, 7.0; Br, 40.0. IR (KBr), ν/cm^{-1} : 1346, 1568 (C–NO₂); 857 (C–Br); 1073, 1100, 3275 (OH); 1463, 2888, 2948, 2966 (CH₂). ¹H NMR (CD_3CN), δ : 3.98 (m, 2 H, OH, the K-part of the ABK-spin system spectrum); 4.16 (m, 4 H, CH₂, the AB-part of the ABK-spin system spectrum).

2-Bromo-2-nitropropane-1,3-diol (2a) was synthesized according to the known procedure⁴ and recrystallized twice from ethyl acetate, m.p. 128–129 °C.

2,2-Dinitropropane-1,3-diol (3) was synthesized according to the known procedure⁹ and recrystallized twice from dichloroethane, m.p. 139–140 °C.

X-ray diffraction study. Crystals of $\text{NaC}_3\text{H}_4\text{NO}_4 \cdot 2\text{H}_2\text{O}$ (**1**) are triclinic, $a = 9.086(3)$ Å, $b = 6.305(3)$ Å, $c = 6.839(5)$ Å, $\alpha = 104.49(5)^\circ$, $\beta = 99.40(5)^\circ$, $\gamma = 77.46(3)^\circ$, $V = 367.8(6)$ Å³, $d_{\text{calc}} = 1.598(2)$ g cm⁻³, $\lambda = 0.7107$ Å; space group $P\bar{1}$, $Z = 2$, $M = 177.09$.

Crystals of $\text{C}_3\text{H}_6\text{BrNO}_4$ (**2**) are monoclinic, $a = 8.053(2)$ Å, $b = 9.677(3)$ Å, $c = 8.989(2)$ Å, $\beta = 90.88(2)^\circ$, $V = 700.5(5)$ Å³, $d_{\text{calc}} = 1.895(2)$ g cm⁻³, $\lambda = 0.7107$ Å; space group Cc , $Z = 4$, $M = 200.00$.

Crystals of $\text{C}_3\text{H}_6\text{BrNO}_4$ (**2a**) are monoclinic, $a = 8.027(3)$ Å, $b = 9.661(3)$ Å, $c = 8.963(5)$ Å, $\beta = 88.99^\circ$, $V = 695.1(6)$ Å³, $d_{\text{calc}} = 1.910(3)$ g cm⁻³, $\lambda = 0.7107$ Å; space group Cc , $Z = 4$, $M = 200.00$.

The intensities of 1050 (**1**), 686 (**2**), and 769 (**2a**) observed independent reflections were measured in the range 0.02 ≤

Table 2. Atomic coordinates ($\times 10^4$) in the structure of **1**

Atom	x	y	z
Na(1)	9275(2)	969(6)	7598(6)
O(1)	3765(6)	8081(9)	7980(9)
O(2)	2775(6)	4972(9)	6679(9)
O(3)	7969(6)	4682(9)	7177(9)
O(4)	6808(6)	1129(9)	8179(9)
O(5)	10235(6)	-2539(8)	8645(9)
O(6)	11516(6)	870(9)	6156(9)
N(1)	5513(7)	2152(9)	7008(9)
C(1)	4007(8)	5874(10)	7407(10)
C(2)	5348(9)	4673(10)	7579(10)
C(3)	6717(8)	5785(10)	8297(10)
H(1)	6406(15)	7400(25)	8291(25)
H(2)	7014(15)	5823(25)	9762(25)
H(3)	6676(20)	1103(35)	9356(35)
H(4)	7741(25)	4534(35)	6009(35)
H(5)	9386(25)	-1723(35)	8632(35)
H(6)	9756(20)	-3533(35)	8314(35)

Table 3. Atomic coordinates ($\times 10^4$) in the structure of **2**

Atom	x	y	z
Br(1)	8966(4)	1001(4)	6926(4)
O(1)	6602(6)	3690(5)	4609(6)
O(2)	7631(6)	4076(5)	7425(6)
O(3)	9000(6)	3302(6)	3385(6)
O(4)	10227(7)	1487(6)	4119(6)
N(1)	9196(7)	2432(7)	4271(7)
C(1)	6441(8)	2321(6)	5291(8)
C(2)	8305(9)	2429(6)	5636(9)
C(3)	8549(8)	3921(6)	6355(8)
H(1)	9639(25)	4135(20)	6551(25)
H(2)	8364(25)	4712(20)	5628(25)
H(3)	7053(25)	4473(20)	8348(25)
H(4)	5860(25)	1651(20)	4718(25)
H(5)	5356(25)	2325(20)	6171(25)
H(6)	5911(25)	4643(20)	4327(25)

Table 4. Atomic coordinates ($\times 10^4$) in the structure of **2a**

Atom	x	y	z
Br(1)	8032(2)	0999(2)	2784(2)
O(1)	5208(4)	1031(3)	5344(4)
O(2)	9365(4)	4166(3)	3253(4)
O(3)	9381(4)	1501(3)	5651(4)
O(4)	7974(4)	3280(3)	6436(4)
N(1)	8298(4)	2398(4)	5505(4)
C(1)	7311(5)	2461(3)	4103(5)
C(2)	7612(6)	3858(4)	3376(6)
C(3)	5462(5)	2283(3)	4540(5)
H(1)	5104(15)	3095(11)	5245(15)
H(2)	4829(15)	2474(12)	3686(15)
H(3)	7251(15)	3808(12)	2283(15)
H(4)	6952(15)	4600(12)	3814(15)
H(5)	9987(15)	3865(12)	2585(15)
H(6)	4166(15)	861(12)	5979(15)

Table 4. Atomic coordinates ($\times 10^4$) in the structure of **3**

Atom	x	y	z
O(1)	3841(2)	4228(2)	5509(3)
O(2)	3477(2)	4522(2)	11219(3)
O(3)	5939(3)	2824(3)	11988(5)
O(4)	4696(6)	1715(2)	10009(6)
O(5)	6975(4)	2881(4)	6927(7)
O(6)	6910(3)	4773(4)	7498(7)
N(1)	5273(3)	2633(3)	10382(5)
N(2)	6457(3)	3785(4)	7646(5)
C(1)	4026(3)	3295(3)	6993(5)
C(2)	5060(3)	3650(3)	8760(5)
C(3)	4704(3)	4750(2)	10022(5)
H(1)	4529(35)	5410(27)	9052(30)
H(2)	3747(35)	4333(35)	12714(98)
H(3)	4331(39)	2574(26)	6211(40)
H(4)	5431(40)	5027(22)	11076(94)
H(5)	3515(35)	4725(22)	5943(54)
H(6)	3090(35)	3190(22)	7800(55)

$\sin\theta/\lambda \leq 0.5$ on a four-circle KM-4 (KUMA-Diffraction, Poland) diffractometer (the $\omega/2\theta$ scanning technique). Structures of **1**, **2**, and **2a** were solved by the direct method using the SHELX-86 program package on a personal computer (SATO).

Atomic coordinates in the structures of **1**, **2**, and **2a** (Tables 2, 3, and 4, respectively) were refined by the full-matrix least squares method using anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms to

$R_1 = 0.063$, $R_2 = 0.076$, $R_{2a} = 0.065$. Atomic coordinates of hydrogen atoms were located from the difference electron density synthesis.

Crystals of $C_3H_6N_2O_6$ (**3**)⁹ are rhombic, $a = 9.767(2)$ Å, $b = 11.253(3)$ Å, $c = 6.076(2)$ Å, $V = 667.8(4)$ Å³, $d = 1.651(2)$ g cm⁻³, $\lambda = 1.5418$ Å, space group $P2_12_12_1$, $Z = 4$, $M = 166.09$. The intensities of 600 observed independent reflections with $I \geq 2.5\sigma(I)$ were measured in the range $0.06 \leq \sin\theta/\lambda \leq 0.618$ on a DAR-UM diffractometer. Structure of **3** was solved by the direct method using the ROENTGEN-76 (BESM-6) program package, $R_3 = 0.058$. Atomic coordinates in the structure of **3** are listed in Table 5.

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