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X-RAY STRUCTURAL INVESTIGATION OF GOSSYPOL AND ITS DERIVATIVES
XXIV. STRUCTURE OF A CLATHRATE OF DIANILINEGOSSYPOL WITH 1,2-DICHLOROETHANE

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The crystal structure of the 1:2 clathrate of dianilinegossypol with 1,2-dichloroethane, which is unstable under ordinary conditions, has been determined. In the clathrate there are two systems of mutually perpendicular channels in which two crystallographically different molecules of the guest are arranged. No intermolecular H bonds of the host-guest type are observed in the structure of the clathrate.

We are making a systematic investigation of the change in the clathrate-forming properties of gossypol on its chemical modification. With this aim, we have studied the recrystallization of dianilinegossypol — the product of the condensation of gossypol with aniline [1] — from solutions in various solvents [2]. This gossypol derivative gives clathrates with all 30 of the solvents tested, 15 of which it has been possible to obtain in the form of single crystals. On the basis of a determination of their crystallographic parameters, these 15 clathrates have been assigned to 10 different isostructural groups. The structure of only one group (group B) has been determined previously, namely: the H-clathrate of dianilinegossypol with ethyl acetate [3]. In the present communication we discuss the structure of the complex of dianilinegossypol with 1,2-dichloroethane, which belongs to a different group (group C) of isostructural clathrates [2, 4].

With 1,2-dichloroethane, dianilinegossypol forms a clathrate having the 1:2 composition, which decomposes under ordinary conditions. The first molecule is present in the quinoid tautomeric form (Fig. 1). The naphthyl nuclei *AB* and *CD* are practically planar — the greatest deviations from the mean square plane of these rings are shown shown by the C7 and C18 atoms, respectively (0.07 Å in each case). The dihedral angle between these rings amounts to 91.9°. The coplanarity of the atoms of the benzene ring *F* is close to ideal: the deviations of the atoms from the mean square plane of the ring do not exceed 0.007 Å. The planarity of the benzene ring *E* of the other aniline substituent of the molecule is also almost ideal (the greatest deviation amounts to 0.01 Å). Ring *F* inclined relative to the naphthyl nucleus *CD* by 13%, while the inclination of ring *E* relative to the *AB* nucleus is three times larger (42°). The values of these angles are determined by the simultaneous action of three factors. The plane-trigonal (instead of pyramidal) configuration of the N1 and N2 nitrogen atoms and the distribution of bond lengths in the C8,C22,N1,C31, and C18,C27,N2,C37 fragments (Table 1) show conjugation of the bonds in these chains of atoms. The delocalization of the electron density in these chains would be ideal if the planes of the corresponding naphthyl and aniline rings were parallel. However, this is prevented by repulsion between the C36 and C22 atoms of the first half (Table I *AB* ring) of the molecule and the C38 and C27 atoms in the second (*CD* ring) half. Even with the observed inclination, the nonvalent distances C36···C22 (2.98 Å) and C38···C27 (3.01 Å) are considerably shortened in comparison with the normal Van der Waals contact of 3.42 Å [5]. And, finally, the crystal field (packing effect) affects the result of competition between these two factors.

The orientations of the isopropyl groups of the two halves of the molecule are the same, namely: the central hydrogen atom of each isopropyl group is directed towards a hydrogen atom of the aromatic system. In the dianilinegossypol molecule, H bonds of two types are observed: the O3···H−N1 H-bond closes the 6-membered membered ring C7−C8−C22−N1−H···03, and the other H-bond, O4−H···O3, closes the 5-membered ring C6−C7−O3···H−04. There

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TABLE 1. Interatomic Distances (Å) in the Structure of the 1:2 Clathrate of Dianilinegossypol with 1,2-Dichloroethane

C(1)—C(2)	1.39 (1)	C(1)—C(9)	1.40 (1)
C(1)—O(1)	1.38 (1)	C(2)—C(3)	1.39 (1)
C(2)—C(12)	1.51 (1)	C(3)—C(4)	1.38 (1)
C(3)—C(21)	1.51 (1)	C(4)—C(10)	1.41 (1)
C(5)—C(6)	1.33 (1)	C(5)—C(10)	1.47 (1)
C(5)—C(23)	1.52 (1)	C(6)—C(7)	1.46 (2)
C(6)—O(4)	1.37 (1)	C(7)—C(8)	1.43 (1)
C(7)—O(3)	1.27 (1)	C(8)—C(9)	1.48 (1)
C(8)—C(22)	1.39 (2)	C(9)—C(10)	1.42 (1)
C(22)—N(1)	1.33 (1)	C(23)—C(24)	1.54 (2)
C(23)—C(25)	1.52 (2)	N(1)—C(31)	1.41 (2)
C(31)—C(32)	1.34 (2)	C(31)—C(36)	1.40 (2)
C(32)—C(33)	1.35 (2)	C(33)—C(34)	1.38 (2)
C(34)—C(35)	1.33 (3)	C(35)—C(36)	1.39 (2)
C(11)—C(12)	1.37 (1)	C(11)—C(19)	1.41 (1)
C(11)—O(5)	1.36 (2)	C(12)—C(13)	1.42 (2)
C(13)—C(14)	1.35 (1)	C(13)—C(26)	1.52 (1)
C(14)—C(20)	1.42 (1)	C(15)—C(16)	1.34 (1)
C(15)—C(20)	1.47 (1)	C(15)—C(28)	1.51 (2)
C(16)—C(17)	1.44 (2)	C(16)—O(8)	1.39 (1)
C(17)—C(18)	1.42 (1)	C(17)—O(7)	1.28 (1)
C(18)—C(19)	1.46 (1)	C(18)—C(27)	1.41 (2)
C(19)—C(20)	1.42 (2)	C(27)—N(2)	1.31 (1)
C(28)—C(29)	1.50 (2)	C(28)—C(30)	1.55 (2)
C(37)—C(38)	1.35 (2)	C(37)—C(42)	1.38 (1)
C(37)—N(2)	1.41 (2)	C(38)—C(39)	1.39 (2)
C(39)—C(40)	1.38 (1)	C(40)—C(41)	1.35 (2)
C(41)—C(42)	1.35 (2)	C(43)—C(44)	1.21 (4)
C(43)—Cl(2)	1.77 (3)	C(44)—Cl(1)	1.87 (3)
C(47)—C(48)	1.30 (7)	C(47)—Cl(3)	1.46 (5)
C(48)—Cl(4)	1.58 (3)		

TABLE 2. Valence Angles in the Structure of the 1:2 Clathrate of Dianilinegossypol with 1,2-Dichloroethane

C(2)—C(1)—C(9)	123.1 (9)	C(2)—C(1)—O(1)	118.6 (7)
C(9)—C(1)—O(1)	118.3 (8)	C(1)—C(2)—C(3)	119.3 (8)
C(1)—C(2)—C(12)	118.5 (9)	C(3)—C(2)—C(12)	122.1 (8)
C(2)—C(3)—C(4)	119.5 (8)	C(2)—C(3)—C(21)	120.4 (8)
C(4)—C(3)—C(21)	120.0 (9)	C(3)—C(4)—C(10)	121.6 (9)
C(6)—C(5)—C(10)	119.2 (9)	C(6)—C(5)—C(23)	119.9 (8)
C(10)—C(5)—C(23)	120.9 (8)	C(5)—C(6)—C(7)	123.6 (9)
C(5)—C(6)—O(4)	124.5 (9)	C(7)—C(6)—O(4)	111.8 (8)
C(6)—C(7)—C(8)	118.9 (8)	C(6)—C(7)—O(3)	116.9 (8)
C(8)—C(7)—O(3)	124.2 (9)	C(7)—C(8)—C(9)	118.2 (8)
C(7)—C(8)—C(22)	118.0 (8)	C(9)—C(8)—C(22)	123.7 (8)
C(1)—C(9)—C(8)	123.8 (8)	C(1)—C(9)—C(10)	116.6 (8)
C(8)—C(9)—C(10)	119.6 (7)	C(4)—C(10)—C(5)	120.1 (9)
C(4)—C(10)—C(9)	119.8 (7)	C(5)—C(10)—C(9)	120.1 (8)
C(8)—C(22)—N(1)	122.8 (9)	C(5)—C(23)—C(24)	111.3 (10)
C(5)—C(23)—C(25)	112.3 (10)	C(24)—C(23)—C(25)	112.1 (9)
C(22)—N(1)—C(31)	124.5 (9)	N(1)—C(31)—C(32)	124.2 (11)
N(1)—C(31)—C(36)	116.6 (13)	C(32)—C(31)—C(36)	119.2 (11)
C(31)—C(32)—C(33)	121.4 (13)	C(32)—C(33)—C(34)	120.0 (18)
C(33)—C(34)—C(35)	120.3 (16)	C(34)—C(35)—C(36)	120.3 (16)
C(31)—C(36)—C(35)	118.6 (15)	C(12)—C(11)—C(19)	123.0 (11)
C(12)—C(11)—O(5)	119.8 (8)	C(19)—C(11)—O(5)	117.2 (8)
C(2)—C(12)—C(11)	120.9 (11)	C(2)—C(12)—C(13)	119.7 (8)
C(11)—C(12)—C(13)	119.3 (8)	C(12)—C(13)—C(14)	118.7 (9)
C(12)—C(13)—C(26)	120.1 (8)	C(14)—C(13)—C(26)	121.2 (12)
C(13)—C(14)—C(20)	123.3 (12)	C(16)—C(15)—C(20)	116.7 (11)
C(16)—C(15)—C(28)	120.1 (9)	C(20)—C(15)—C(28)	123.2 (8)
C(15)—C(16)—C(17)	125.4 (9)	C(15)—C(16)—O(8)	120.1 (11)
C(17)—C(16)—O(8)	114.5 (8)	C(16)—C(17)—C(18)	118.1 (8)
C(16)—C(17)—O(7)	117.0 (8)	C(18)—C(17)—O(7)	124.8 (12)
C(17)—C(18)—C(19)	119.6 (11)	C(17)—C(18)—C(27)	115.8 (8)
C(19)—C(18)—C(27)	124.5 (8)	C(11)—C(19)—C(18)	124.2 (11)
C(11)—C(19)—C(20)	117.3 (8)	C(18)—C(19)—C(20)	118.3 (8)
C(14)—C(20)—C(15)	120.1 (11)	C(14)—C(20)—C(19)	118.0 (8)
C(15)—C(20)—C(19)	121.8 (8)	C(18)—C(27)—N(2)	124.7 (8)
C(15(—C(28)—C(29)	113.9 (12)	C(15)—C(28)—C(30)	111.9 (11)
C(29)—C(28)—C(30)	113.3 (11)	C(38)—C(37)—C(42)	119.9 (13)
C(38)—C(37)—N(2)	123.6 (8)	C(42)—C(37)—N(2)	116.5 (10)
C(37)—C(38)—C(39)	120.5 (8)	C(38)—C(39)—C(40)	118.7 (12)
C(39)—C(40)—C(41)	120.1 (16)	C(40)—C(41)—C(42)	121.5 (10)
C(37)—C(42)—C(41)	119.3 (11)	C(27)—N(2)—C(37)	130.3 (8)
C(44)—C(43)—Cl(2)	113.6 (23)	C(43)—C(44)—Cl(1)	109.5 (23)
C(48)—C(47)—Cl(3)	160.8 (24)	C(47)—C(48)—Cl(4)	109.7 (23)

TABLE 3. Coordinates ($\times$ 104; for the hydrogen atoms $\times 10^3$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^2$) in the Structure of the 1:2 Clathrate of Dianilinegossypol with 1,2-Dichloroethane

Atom	*x*	*y*	*z*	U^a
C(1)	306(8)	2283(8)	437(6)	44(6)
C(2)	614(8)	3091(8)	1243(6)	44(5)
C(3)	1592(8)	2664(9)	1584(6)	50(6)
C(4)	2254(8)	1447(8)	1112(6)	47(6)
C(5)	2664(8)	-668(8)	-177(7)	47(6)
C(6)	2291(8)	-1450(9)	-885(7)	47(6)
C(7)	1241(8)	-1095(9)	-1264(7)	46(6)
C(8)	575(8)	157(8)	-872(6)	41(5)
C(9)	932(8)	1035(8)	-50(6)	39((5)
C(10)	1943(8)	619(8)	303(6)	40(5)
C(11)	-1056(8)	4966(8)	2389(6)	42(5)
C(12)	-101(8)	4422(8)	1694(6)	47(5)
C(13)	197(8)	5112(9)	1379(6)	54(6)
C(14)	-467(9)	6295(8)	1781(6)	55(6)
C(15)	-2214(8)	8134(8)	2828(6)	51(6)
C(16)	-3149(8)	8626(8)	3499(6)	48(6)
C(17)	-3476(8)	8020(8)	3904(6)	44(5)
C(18)	-2748(8)	6812(8)	3590(6)	45(5)
C(19)	-1737(8)	6204(8)	2839(6)	45(5)
C(20)	-1475(7)	6877(7)	2485(6)	42(5)
C(21)	1954(10)	3522(10)	2449(7)	80(7)
C(22)	-332(9)	482(9)	-1315(7)	53(6)
C(23)	3829(9)	-1116(9)	123(7)	62(6)
C(24)	4896(9)	-1686(11)	-649(10)	101(9)
C(25)	3796(10)	-1956(12)	463(8)	100(9)
C(26)	1274(9)	4531(9)	625(7)	71(6)
C(27)	-3017(8)	6314(7)	4088(6)	49(5)
C(28)	-1989(10)	8859(9)	2443(8)	79(7)
C(29)	-1691(11)	9936(11)	3141(9)	109(9)
C(30)	-2992(13)	9166(10)	1924(8)	103(9)
O(1)	-664(6)	2729(5)	100(4)	62(4)
O(3)	2881(5)	-2666(5)	-1382(4)	62(4)
O(4)	994(5)	-1938(5)	-1948(4)	57(4)
O(5)	-1367(5)	4306(5)	2682(4)	53(4)
O(7)	-4399(5)	8627(5)	4538(4)	58(4)
O(8)	-3890(5)	9811(5)	3859(4)	60(4)
N(1)	-669(7)	-323(7)	-2037(6)	54(5)
N(2)	-3911(6)	6864(6)	4771(5)	52(4)
C(31)	-1504(9)	-38(10)	-2560(7)	55(6)
C(32)	-1673(10)	882(10)	-2700(8)	72(8)
C(33)	-2479(13)	1103(12)	-3213(10)	99(10)
C(34)	-3145(12)	367(15)	-3618(11)	112(12)
C(35)	-3010(13)	-545(14)	-3490(10)	106(11)
C(36)	-2167(11)	-796(10)	-2971(8)	78(8)
C(37)	-4207(9)	6523(8)	5385(6)	50(6)
C(38)	-3618(8)	5448(10)	5304(7)	62(7)
C(39)	-3976(10)	5161(10)	5920(8)	67(7)
C(40)	-4952(11)	5985(12)	6603(8)	80(8)
C(41)	-5528(11)	7055(11)	6676(8)	88(8)
C(42)	-5188(10)	7336(9)	6073(7)	77(7)
C(43)	5364(23)	-5621(21)	-1436(13)	242(22)
C(44)	4469(22)	-5755(27)	-1748(18)	280(32)
Cl(1)	3372(4)	-5515(5)	-836(3)	155(4)
Cl(2)	6394(5)	-5642(4)	-2189(4)	174(4)
C(47)	-239(30)	2530(33)	5294(23)	422(58)
C(48)	149(17)	3235(28)	5163(12)	306(30)
Cl(3)	-896(10)	2120(12)	5720(8)	403(14)
Cl(4)	-389(8)	3361(8)	4340(6)	335(8)

TABLE 3. (Continued)

Atom	x	y	z
H(431)	511(2)	-485(2)	-87(1)
H(432)	574(2)	-624(2)	-129(1)
H(441)	413(2)	-521(3)	-197(2)
H(442)	469(2)	-657(3)	-226(2)
H(471)	-66(3)	235(3)	478(2)
H(472)	50(3)	188(3)	512(2)
H(481)	-2(2)	401(3)	572(1)
H(482)	100(2)	283(3)	498(1)
H(4)	290(6)	114(6)	145(4)
H(211)	240(8)	329(8)	270(6)
H(212)	142(9)	387(9)	302(7)
H(213)	210(9)	411(9)	233(7)
H(22)	-86(7)	131(7)	-116(5)
H(23)	395(7)	-50(7)	77(5)
H(241)	556(8)	-186(8)	-40(6)
H(242)	501(9)	-244(9)	-112(7)
H(243)	494(10)	-105(11)	-91(8)
H(251)	454(8)	-217(8)	66(6)
H(252)	328(8)	-142(8)	114(6)
H(253)	394(8)	-285(8)	-10(7)
H(32)	-127(7)	142(7)	-236(6)
H(33)	-248(6)	154(6)	-333(5)
H(34)	-372(9)	62(9)	-402(7)
H(35)	-324(10)	-137(10)	-387(8)
H(36)	-215(8)	-136(8)	-272(6)
H(1)o	-90(10)	343(10)	45(8)
H(4)o	242(8)	-301(8)	-170(6)
H(1)n	-8(11)	-112(11)	-223(8)
H(14)	-31(5)	673(5)	159(4)
H(261)	209(7)	433(7)	98(6)
H(262)	98(8)	374(9)	-4(7)
H(263)	110(7)	505(7)	47(6)
H(27)	-256(5)	567(5)	395(4)
H(28)	-144(5)	843(5)	196(4)
H(291)	-208(6)	1027(6)	353(5)
H(292)	-157(9)	1049(9)	290(7)
H(293)	-108(10)	963(10)	364(7)
H(301)	-390(7)	987(7)	257(6)
H(302)	-301(10)	958(10)	163(8)
H(303)	-287(10)	833(11)	139(8)
H(38)	-299(7)	489(7)	489(5)
H(39)	-352(7)	436(7)	586(6)
H(40)	-514(8)	567(8)	700(7)
H(41)	-617(7)	779(7)	732(5)
H(42)	-572(8)	797(8)	592(6)
H(5)o	-99(7)	360(7)	242(6)
H(8)o	-423(6)	999(6)	434(5)
H(2)n	-431(7)	735(7)	482(6)

*$U = \frac{1}{3}\sum_i\sum_j U_{ij}\, a_i^*\, a_j^*\, a_i \cdot a_j$

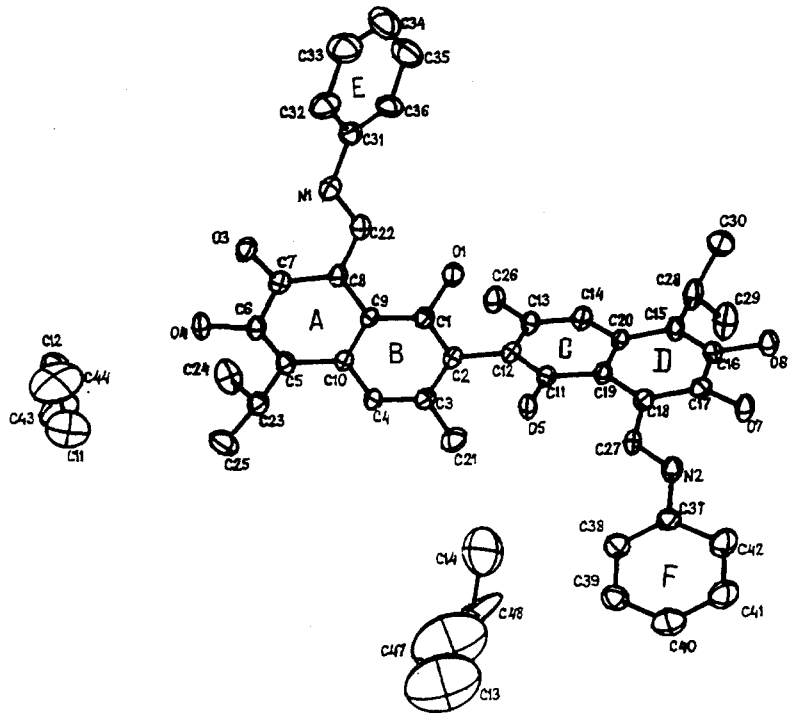

Fig. 1. Independent part of the structure of the 1:2 clathrate of dianiline-gossypol with 1,2-dichloroethane.

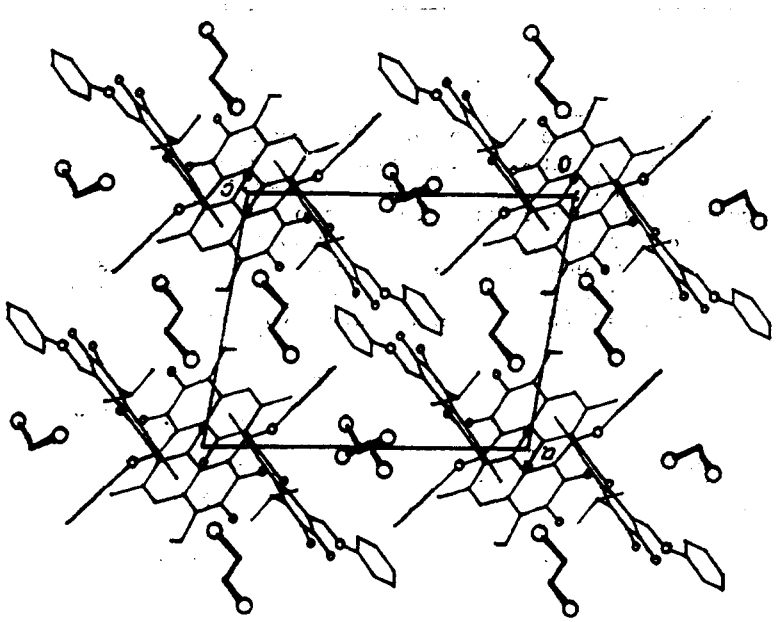

Fig. 2. Crystal structure of the 1:2 clathrate of dianilinegossypol with 1,2-dichloroethane.

are analogous bonds in the other half of the molecule. The lengths of the intramolecular H-bonds differ from those observed in the H-clathrate of dianilinegossypol with ethyl acetate [3] and are close to the values in gossypol cathrates [6, 7, 8]. The same can be said relative to the bond lengths and valence angles (Tables 1 and 2).

One of the two independent molecules of 1,2-dichloroethane has the usual *trans*- conformation (molecule I), while the other (molecule II) is twisted (the Cl−C−Cl torsional angle is close to 90°) under the action of the crystal field.

In crystals of the clathrate of dianilinegossypol with 1,2-dichloroethane, the molecules of the host are united through a O5−H···O3 H-bond, which is characteristic for many crystalline forms of gossypol [5, 7], into centrosymmetric dimers. The length of this bond and the angle at the H atom are 2.71 Å and 147.2°. The dimers are linked with one another likewise by centrosymmetric O8−H···O7 H-bonds 2.79 Å long and with a O−H···O angle of 143°. As a result, columns of molecules parallel to the [12$\bar{1}$] direction are formed (Fig. 2). In the packing of such columns into the crystal, voids of two types appear.. Between the nuclei *CD* and the aniline fragment of the first half there are channels parallel to the *b* axis. Molecules of 1,2-dichloroethane are located in these channels. Two molecules I of the guest are located in cells formed by sections of the two halves of the host molecule and the aniline fragments of the *CD* half. However, these cells are poorly closed in the [10$\bar{1}$] direction and communicate with the channels in which the guest molecules II are located. As a result, other channels running in the [10$\bar{1}$] direction are formed which contain 1,2-dichloroethane molecules of both types. Apparently, the existence of two mutually perpendicular channels explains the extreme instability of the crystals of the clathrate of dianilinegossypol with 1,2-dichloroethane and their rapid decomposition on extraction from their mother solution. The 1,2-dichloroethane molecules have no H-bonds with the host molecules. As a result, the 01−H hydroxy group, which is "sensory" for host−guest H bonds, does not participate in intermolecular H bonds which is observed extremely rarely in the clathrates of gossypol itseslf.

EXPERIMENTAL

Single crystals of the clathrate were grown from solutions of gossypol in 1,2-dichloroethane during reaction with aniline at room temperature. The crystallographic parameters of a single crystal were determined and refined with respect to 15 reflections on a Syntex $P2_1$ automatic four-circle diffractometer:

a=11,996(3) Å	α=119,76(2)°	V=2235,0(1,7)Å^3
b=13,647(3) Å	β=91,07(2)°	d_{calc}=1,29 g/cm^3
c=16,793(5) Å	γ=71,74(2)°	Z=2

Space group P$\bar{1}$.

The intensities of 5298 reflections were measured by the $\theta/2\theta$- scanning method using a graphite monochromator (CuK_α radiation). After allowing for Lorentz and polarization factors and eliminating weak reflections with $F < 4\sigma$, the working group consisted of 2640 reflections. The structure was interpreted by the direct method using the MULTAN-80 program [8] on a IBM-286 PC. The structure was refined by the SHELX-76 program [9] on an IBM-386 PC. The atoms of the molecules of the solvent and the hydrogen atoms were localized in difference Fourier syntheses. The final discrepancy factor was R = 0.076. The coordinates of the atoms are given in Table 3.

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