

Refinement

Refinement on <i>F</i>	$(\Delta/\sigma)_{\max} = 0.003$
<i>R</i> = 0.035	$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
<i>wR</i> = 0.040	$\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$
<i>S</i> = 1.27	Extinction correction: none
2156 reflections	Atomic scattering factors
226 parameters	from <i>International Tables</i>
H atoms riding with fixed	for <i>Crystallography</i> (1992,
$U_{\text{iso}} = 0.1 \text{ \AA}^2$	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F)]$	6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Co	0.45644 (3)	0.19228 (2)	0.61781 (3)	0.042 (1)
O1	0.4687 (1)	0.2759 (1)	0.6820 (1)	0.053 (1)
O2	0.3488 (1)	0.1307 (1)	0.6473 (1)	0.051 (1)
N1	0.5928 (2)	0.1549 (1)	0.6493 (2)	0.039 (1)
N2	0.4141 (2)	0.2085 (1)	0.4942 (2)	0.042 (1)
C1	0.5523 (2)	0.2993 (2)	0.7187 (2)	0.043 (1)
C2	0.5520 (2)	0.3662 (2)	0.7544 (2)	0.052 (2)
C3	0.6356 (3)	0.3941 (2)	0.7936 (2)	0.057 (2)
C4	0.7246 (2)	0.3564 (2)	0.8001 (2)	0.058 (2)
C5	0.7279 (2)	0.2911 (2)	0.7675 (2)	0.048 (2)
C6	0.6432 (2)	0.2606 (2)	0.7256 (2)	0.038 (1)
C7	0.6557 (2)	0.1915 (2)	0.6941 (2)	0.039 (2)
C8	0.6235 (2)	0.0840 (2)	0.6235 (2)	0.049 (2)
C9	0.6150 (3)	0.0763 (2)	0.5252 (2)	0.072 (2)
C10	0.5597 (3)	0.0327 (2)	0.6720 (3)	0.076 (2)
C11	0.2874 (2)	0.1018 (2)	0.5898 (2)	0.045 (2)
C12	0.2203 (2)	0.0504 (2)	0.6200 (2)	0.057 (2)
C13	0.1538 (2)	0.0184 (2)	0.5646 (3)	0.069 (2)
C14	0.1501 (3)	0.0348 (2)	0.4770 (3)	0.071 (2)
C15	0.2140 (2)	0.0846 (2)	0.4445 (2)	0.060 (2)
C16	0.2843 (2)	0.1183 (1)	0.4993 (2)	0.044 (2)
C17	0.3438 (2)	0.1719 (1)	0.4583 (2)	0.048 (2)
C18	0.4577 (3)	0.2651 (2)	0.4396 (2)	0.056 (2)
C19	0.4054 (3)	0.3322 (2)	0.4643 (3)	0.092 (3)
C20	0.5707 (3)	0.2688 (2)	0.4548 (2)	0.068 (2)

Table 2. Selected geometric parameters (\AA , °)

Co—O1	1.901 (2)	N1—C7	1.288 (4)
Co—O2	1.910 (2)	N1—C8	1.489 (4)
Co—N1	1.999 (2)	N2—C17	1.290 (4)
Co—N2	1.984 (2)	N2—C18	1.492 (4)
O1—C1	1.317 (3)	C1—C2	1.408 (4)
O2—C11	1.318 (4)		
O1—Co—O2	118.53 (9)	Co—O2—C11	124.7 (2)
O1—Co—N1	96.35 (9)	Co—N1—C7	120.5 (2)
O1—Co—N2	111.93 (9)	Co—N1—C8	121.2 (2)
O2—Co—N1	112.72 (9)	C7—N1—C8	118.3 (2)
O2—Co—N2	96.43 (9)	Co—N2—C17	121.0 (2)
N1—Co—N2	122.6 (1)	Co—N2—C18	122.3 (2)
Co—O1—C1	125.7 (2)	C17—N2—C18	116.7 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SIMPEL* (Perchar & Schenk, 1987). Program(s) used to refine structure: *MolEN* (Fair, 1990).

The authors wish to acknowledge the purchase of the *CAD-4* diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2436–2439

Aquabis(*p*-nitrosalicylato-*O,O'*)lead(II)

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(Received 1 November 1995; accepted 30 May 1996)

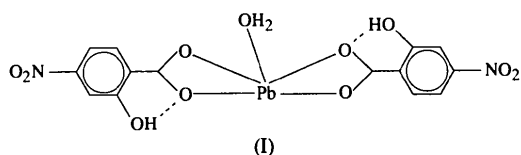
Abstract

In the crystal structure of the title compound, [Pb(C₇H₄NO₅)₂(H₂O)], the sevenfold coordination around the Pb atom consists of four O atoms from two chelating carboxylate groups, one water O atom and two additional O atoms belonging to a carboxyl and a hydroxy group of neighbouring molecules. The Pb—O distances are in the range 2.419(4)–3.084(5) Å, the shortest distance being to a water O atom. Two intramolecular and two intermolecular hydrogen bonds are also observed in the polymeric structure.

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Comment

Structures of lead(II) complexes with different substituents at the *ortho* or *para* positions of benzoate ligands, *e.g.* diaquabis(*p*-nitrobenzoato)lead(II) (Usubaliev, Amirov, Amiraslanov & Mamedov, 1989), monoaquabis(*p*-hydroxybenzoato)lead(II) (Dzhafarov, Amiraslanov, Nadzhafov, Movsumov & Mamedov, 1981) and aquabis(salicylato)lead(II) (Usubaliev *et al.*, 1987), have been reported previously. The title compound, (I), was synthesized in order to study the structure of a lead(II) complex with benzoate ligands containing *p*-nitro and *o*-hydroxy groups simultaneously.



The coordination of the Pb atom involves three primary bonds to carboxyl O1 [2.452 (4) Å], carboxyl O6 [2.428 (5) Å] and aqua O11 atoms [2.419 (3) Å], while secondary interactions with carboxyl O2 [2.691 (4) Å] and O7 atoms [2.727 (5) Å] of the same molecule complete the chelate rings (Fig. 1). Two additional weaker intermolecular contacts with carboxyl O7ⁱ [2.872 (5) Å] and hydroxy O5ⁱⁱ atoms [3.084 (5) Å] increase the coordination number to seven [symmetry codes: (i) 1 + x, y, z; (ii) 1 - x, 1 - y, 1 - z]. All other O atoms are more than 3.35 Å from the Pb atom. This seven-coordinate geometry is highly irregular and leaves a substantial

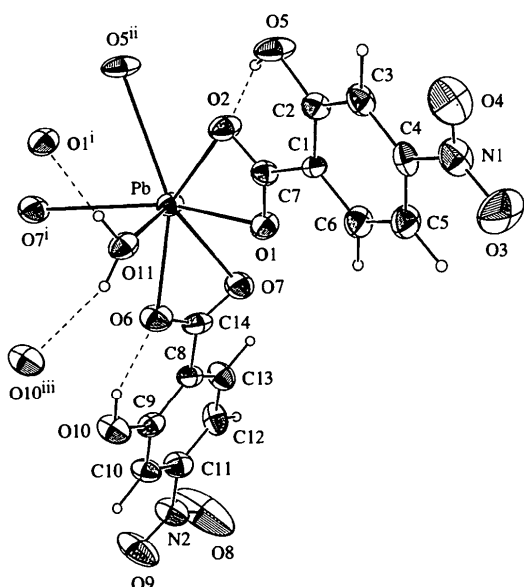


Fig. 1. The molecular structure of (I) with the atom-numbering scheme and ellipsoids drawn at the 50% probability level. H atoms are shown with arbitrary radii. Connections are shown to adjacent units to complete the Pb coordination and hydrogen bonding. The symmetry codes are labelled as in the *Comment* section.

'empty' region on one side of the Pb atom, which can be attributed to a stereochemically-active lone pair of electrons, typical for Pb^{II}.

The two hydroxy groups in the molecule, O5 and O10, are involved in intramolecular hydrogen bonds to the carboxyl O2 and O6 atoms, respectively. The water molecule is involved in two intermolecular hydrogen bonds to the carboxyl O1ⁱ and hydroxy O10ⁱⁱⁱ atoms, so that Pb atoms are cross-linked by a variety of direct covalent and hydrogen-bond interactions [symmetry code: (iii) 1 - x, 1 - y, -z]. Details of the hydrogen-bonding geometry are given in Table 3 and Fig. 2 shows the packing.

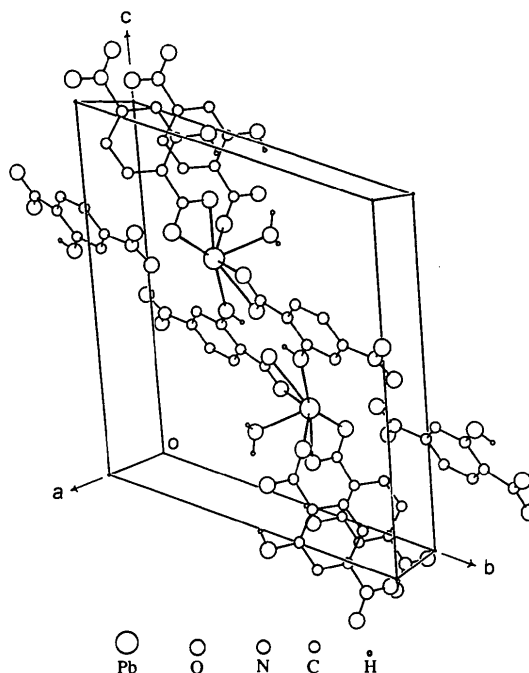


Fig. 2. Part of the polymeric structure with a view direction inclined to the shortest cell axis.

A comparison of compound (I) with the related compounds mentioned above indicates that the Pb²⁺ cation forms a monomeric structure with *p*-nitrobenzoic acid (Usubaliev *et al.*, 1989), but a dimeric structure with *p*-hydroxybenzoic acid (Dzhafarov *et al.*, 1981). The crystal structure of aquabis(salicylato)lead(II) (Usubaliev *et al.*, 1987) consists of polymeric helices. The electronic (and possibly steric) properties of the substituents thus seem to play a significant role in the structure formation. Distortions of coordination polyhedra are partly due to the formation of chelate rings with RCO₂ groups and are also influenced strongly by inert lone-pair effects. The coordination numbers in these complexes lie between six and eight, and the Pb—O separations are in the range 2.35 (7)–3.07 (3) Å. The coordination number and Pb—O distances in the present structure are consistent with previous observations.

Experimental

The title compound was synthesized by the reaction of hot aqueous solutions of Pb(NO₃)₂ and sodium *p*-nitrosalicylate in a 1:2 stoichiometric ratio. The mixture was filtered and crystals were obtained after a few days at room temperature.

Crystal data

[Pb(C₇H₄NO₅)₂(H₂O)] $M_r = 589.433$

Triclinic

 $P\bar{1}$ $a = 4.8797(11) \text{ \AA}$ $b = 12.1550(10) \text{ \AA}$ $c = 14.7338(16) \text{ \AA}$ $\alpha = 68.364(10)^\circ$ $\beta = 86.482(12)^\circ$ $\gamma = 78.770(11)^\circ$ $V = 796.68(19) \text{ \AA}^3$ $Z = 2$ $D_x = 2.457 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer

 $\omega/2\theta$ scans

Absorption correction:

empirical via ψ scans

(MolEN; Fair, 1990)

 $T_{\min} = 0.069$, $T_{\max} = 0.98$

3610 measured reflections

2822 independent reflections

Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 9.92\text{--}18.12^\circ$ $\mu = 10.73 \text{ mm}^{-1}$ $T = 295 \text{ K}$

Irregular

 $0.35 \times 0.20 \times 0.10 \text{ mm}$

Orange

2725 observed reflections

 $[I > 3\sigma(I)]$ $R_{\text{int}} = 0.021$ $\theta_{\text{max}} = 26.32^\circ$ $h = 0 \rightarrow 6$ $k = -14 \rightarrow 15$ $l = -18 \rightarrow 18$

3 standard reflections

frequency: 120 min

intensity decay: 0.9%

Refinement

Refinement on F $R = 0.027$ $wR = 0.029$ $S = 0.88$

2395 reflections

253 parameters

H atoms riding with $U(\text{H}) =$ $1.3U_{\text{eq}}(\text{C/O})$ $w = 1/\sigma^2(F)$ $(\Delta/\sigma)_{\text{max}} = 0.0006$ $\Delta\rho_{\text{max}} = 0.814 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -1.025 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from International Tables

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Pb	0.35950 (6)	0.37081 (2)	0.32420 (2)	2.204 (4)
O1	-0.0242 (9)	0.5389 (4)	0.3134 (3)	2.61 (9)
O2	0.2808 (9)	0.5216 (4)	0.4229 (3)	2.9 (1)
O3	-0.6471 (12)	1.0940 (5)	0.3274 (4)	5.0 (2)
O4	-0.3232 (12)	1.0801 (4)	0.4265 (4)	4.2 (1)
O5	0.2351 (10)	0.6750 (4)	0.5077 (3)	3.3 (1)
O6	0.2464 (10)	0.3930 (4)	0.1594 (3)	3.1 (1)
O7	-0.0837 (10)	0.3143 (4)	0.2579 (3)	3.1 (1)
O8	-0.3967 (17)	0.0829 (6)	-0.0777 (5)	11.2 (2)
O9	-0.1169 (13)	0.1690 (5)	-0.1737 (4)	6.2 (1)
O10	0.2542 (9)	0.4056 (4)	-0.0190 (3)	3.2 (1)
O11	0.5198 (9)	0.5505 (4)	0.2170 (3)	2.6 (1)
N1	-0.4430 (10)	1.0381 (5)	0.3791 (4)	3.0 (1)
N2	-0.2222 (13)	0.1432 (5)	-0.0970 (4)	3.4 (1)

C1	-0.0838 (12)	0.6914 (5)	0.3817 (4)	2.0 (1)
C2	0.0150 (13)	0.7376 (5)	0.4452 (4)	2.2 (1)
C3	-0.1037 (14)	0.8509 (5)	0.4460 (4)	2.4 (1)
C4	-0.3260 (13)	0.9152 (5)	0.3836 (4)	2.3 (1)
C5	-0.4377 (14)	0.8732 (6)	0.3210 (5)	2.8 (1)
C6	-0.3103 (14)	0.7603 (6)	0.3217 (5)	2.7 (1)
C7	0.0674 (13)	0.5763 (5)	0.3733 (4)	2.1 (1)
C8	-0.0238 (13)	0.2860 (5)	0.1061 (4)	2.3 (1)
C9	0.0793 (13)	0.3239 (5)	0.0119 (4)	2.4 (1)
C10	0.0125 (14)	0.2768 (6)	-0.0546 (4)	2.6 (1)
C11	-0.1525 (15)	0.1915 (6)	-0.0242 (5)	3.0 (1)
C12	-0.2603 (15)	0.1489 (6)	0.0688 (5)	3.2 (2)
C13	-0.1935 (15)	0.2006 (6)	0.1322 (5)	3.0 (2)
C14	0.0447 (14)	0.3342 (6)	0.1795 (4)	2.6 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pb—O1	2.452 (4)	Pb—O11	2.419 (4)
Pb—O2	2.691 (4)	O1—C7	1.269 (9)
Pb—O5 ⁱ	3.084 (5)	O2—C7	1.235 (7)
Pb—O6	2.428 (5)	O6—C14	1.284 (9)
Pb—O7	2.727 (5)	O7—C14	1.246 (7)
Pb—O7 ⁱⁱ	2.872 (5)		
O1—Pb—O2	50.1 (2)	O2—Pb—O5 ⁱ	60.7 (1)
O1—Pb—O6	89.1 (1)	O11—Pb—O5 ⁱ	94.5 (1)
O1—Pb—O7	75.9 (2)	O6—Pb—O7 ⁱⁱ	81.3 (2)
O1—Pb—O11	74.2 (1)	O7—Pb—O7 ⁱⁱ	121.2 (2)
O2—Pb—O6	133.9 (2)	O11—Pb—O7 ⁱⁱ	68.7 (2)
O2—Pb—O7	120.9 (2)	O5 ⁱ —Pb—O7 ⁱⁱ	72.6 (2)
O2—Pb—O11	74.6 (2)	Pb—O1—C7	99.2 (3)
O6—Pb—O7	50.5 (2)	Pb—O6—C14	98.5 (4)
O6—Pb—O11	73.9 (2)	O1—C7—O2	121.7 (6)
O1—Pb—O5 ⁱ	110.5 (1)	O6—C14—O7	122.3 (7)
Pb—O1—C7—O2	-6.3 (6)	Pb—O6—C14—O7	19.3 (7)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O5—H5 ⁱ ...O2	0.827 (5)	1.791 (5)	2.572 (7)	156.4 (3)
O10—H10 ⁱ ...O6	0.873 (5)	1.808 (7)	2.575 (8)	144.8 (4)
O11—H11 ⁱ ...O1 ⁱ	0.822 (5)	1.848 (4)	2.666 (6)	173.4 (3)
O11—H11 ⁱⁱ ...O10 ⁱⁱ	0.878 (5)	2.118 (5)	2.948 (7)	157.6 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, -z$.

The high degree of anisotropy observed for the N2 nitro group indicates possible disorder, but this could not be resolved. The largest positive and negative features in the final difference map lie within 1 \AA of the Pb atom.

Data collection: CAD-4 Express (Enraf–Nonius, 1993). Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SIMPEL in MolEN. Program(s) used to refine structure: LSFM in MolEN. Molecular graphics: ORTEP (Johnson, 1965) in MolEN. Software used to prepare material for publication: MolEN.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2439–2441

Bis[$(\mu$ -2,6-diphenylphenoxido-*O*:*O*)diethylgallium]

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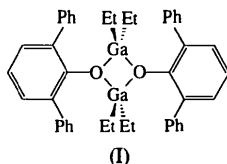
(Received 29 March 1996; accepted 6 June 1996)

Abstract

The title compound, $[\text{Ga}_2(\text{C}_{18}\text{H}_{13}\text{O})_2(\text{C}_2\text{H}_5)_4]$, contains discrete dimeric molecules containing an essentially planar four-membered (Ga—O—Ga—O) ring [O—Ga—O 75.04 (7) and 75.99 (7)°]. The Ga—O bond distances range from 1.992 (2) to 2.034 (2) Å and the O atoms have a trigonal-planar coordination.

Comment

There has been much interest in compounds of the alkylaluminium species with sterically bulky aryloxo ligands as reagents for new applications in organic synthesis and catalysis (Healy, Power & Barron, 1994). Some studies have been extended to gallium-containing molecules, with monomeric (Petrie, Olmstead & Power, 1991; Cleaver & Barron, 1993) and dimeric species having been reported. As part of a study on gallium-oxo species, we have studied the bulky 2,6-diphenylphenoxide ligand with the ethyl gallium residue. The four-membered ring found in the present dimeric compound, (I), has been found before, notably by Cleaver,



Barron, McGufey & Bott (1994), who reported seven derivatives with *tert*-butyl gallium.

The crystal structure of the title compound is found to contain discrete dimeric molecules containing a four-membered (Ga—O—Ga—O) ring (Fig. 1). The (Ga—O—Ga—O) ring is essentially planar [maximum deviation from the plane through the four atoms is 0.010 (1) Å], with smaller O—Ga—O ring angles [O—Ga—O 75.04 (7) and 75.99 (7)°] and correspondingly larger Ga—O—Ga angles than reported previously (Cleaver *et al.*, 1994). The Ga—O distances are in good agreement with earlier work on dimeric species (being longer than the monomeric values) and the geometry at the Ga atom is distorted tetrahedral (see Table 2). The Ga—C distances [1.961 (3)–1.971 (3) Å] are within the expected range (Hahn, Schneider & Reier, 1990).

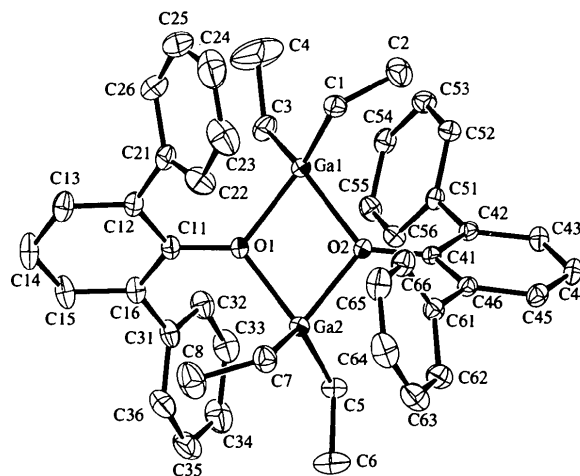


Fig. 1. The molecular structure of $[\text{Et}_2\text{Ga}(\text{OC}_{18}\text{H}_{13})]_2$ showing the labelling scheme, with displacement ellipsoids drawn at the 30% probability level. H atoms have been excluded for clarity.

The O atoms are in a trigonal-planar environment as has been noted before both in gallium-containing alkoxides (Cleaver *et al.*, 1994) and other μ_2 -alkoxides. The phenoxide C₆ rings are neither parallel nor perpendicular to the Ga₂O₂ ring, but make an average Ga—O—C—C torsion angle of -54° .

The title molecule has approximate *D*₂ point group symmetry.

Experimental

Working under argon, the title compound was prepared by slow addition of GaEt₃ (4.1 mmol) dissolved in toluene to a cold (210 K) solution of 2,6-diphenylphenol (4.1 mmol) in toluene. The solution was allowed to warm slowly to room temperature with stirring for 5 h. Removal of the volatiles gave the required product and colourless crystals were obtained from toluene.