Structure characterisation of the organoaluminium intermediate resulting from the alkylation of a chelated carbonyl group. Molecular structure of the trinuclear [MeAl][C$_{12}$H$_{20}$O$_4$][AlMe$_2$]$_2$ compound

Janusz Lewinski *, Janusz Zachara

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Abstract

The interaction of Me$_3$Al with Me$_2$Al(acac) results in the carbonyl alkylation of the chelating acetylacetonate ligand and formation of trinuclear complex [MeAl][C$_{12}$H$_{20}$O$_4$][AlMe$_2$]$_2$ (1). The title compound has been characterised by ^{1}H-and ^{27}Al-NMR spectroscopy. The ^{1}H-NMR spectra are consistent with the presence of two distinct isomers in an equimolar ratio: *cis*-1 and *trans*-1. Both isomers contain two methylated acac units bridged by three organoaluminium moieties: central five-coordinated methyl aluminium species and two terminal four-coordinated dimethylaluminium species. The structure of *cis*-1 has been confirmed by X-ray crystallography which revealed that the five-coordinated aluminium atom rises in almost ideal square pyramidal geometry. The role of the molar ratio of reactants is discussed. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Aluminium; Carbonyl alkylation; Crystal structure

1. Introduction

Alkylation of the carbonyl group by organometallic compounds has become one of the most important reactions in the C–C bond formation in organic synthesis [1,2]. Particular interest has been focused on the diastereoselective addition of alkyl groups to a carbonyl compound with a chiral centre. The chelation control products are usually rationalised solely on the basis of the stereochemical outcome [3]. Attention is mainly drawn towards the organic final products, and the intermediate stages of these reactions are known only to a small extent. At a lack of knowledge of the structure of the organometallic products formed at particular stages of the carbonyl group alkylation, the reactant mole ratios are usually chosen experimentally. In view of controlling these reactions it has become very important to characterise the intermediate metal

chelates. Earlier in our laboratory the reactions of dialkyl- and dichloroaluminium acetylacetonates with Lewis bases have been studied [4]. Recently we have undertook extensive studies on the structure and reactivity of alkylaluminium chelate complexes derived from reactions of aluminium alkyls with bifunctional carbonyl compounds [5]. As part of this work we describe here the reinvestigation of the alkylation of chelated acetylacetonate ligand by Me$_3$Al. The early work of Kroll at al. [6] suggested that the alkylation of the carbonyl group in acac ligand occurs with an organoaluminium compound formation of the following stoichiometry Me$_2$Al–OC(CH$_3$)$_2$CH=C(CH$_3$)O–AlMe$_2$.

2. Results and discussion

The addition of Me$_3$Al to a hexane solution of Me$_2$Al(acac) results in alkylation of the coordinated carbonyl group and formation of the trinuclear complex [MeAl][(acac-Me)$_2$][AlMe$_2$]$_2$ (1).

* Corresponding author. Tel.: +48 22 6607315; fax: +48 22 6607279; e-mail: lewin@ch.pw.edu.pl

$$2Me_2Al(acac) + Me_3Al \rightarrow [AlMe][(acac-Me)_2][AlMe_2]_2 \tag{1}$$
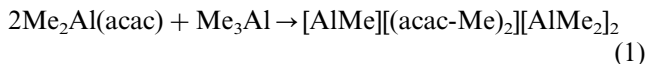
When the reactant molar ratio is according to Eq. (1), the formation of **1** proceeds slowly at 30°C and the reaction is completed within 8 h. In these conditions a small amount of some additional compounds are formed which has been detected in the ^{1}H-NMR spectrum of the crude product. It should be noted that carbonyl alkylation proceeds easier when an excess of Me_3Al was used. For an equimolar ratio of reactants the reactions were completed in 1 h under the same condition and **1** was obtained almost quantitatively; Me_3Al excess was easily removed with the solvent by evaporation in vacuo. Thus, the required stoichiometry for this C-nucleophile addition corresponds to the composition of **1** and an excess of Me_3Al only increases the rate of the addition reaction. The ^{1}H-NMR spectrum of the crude product revealed that it consists of an equimolar mixture of two geometrical isomers: **1**-*cis* and **1**-*trans*, with respect to the deposition of the methylated acetylacetonate ligands (acac-Me) (Scheme 1). Both isomers contain two acac-Me units bridged by three organoaluminium moieties: central five-coordinated methylaluminium species and two terminal four-coordinated dimethylaluminium species. In the isomer **1**-*cis*, the terminal aluminium atoms join two alkoxide oxygens or two enolate oxygen atoms, respectively, while in the isomer **1**-*trans* each of the terminal aluminium atoms is bonded to one alkoxide and one enolate oxygen atoms. The isomers of **1** may be readily separated by fractional crystallisation from hexane. In Fig. 1a is shown the ^{1}H-NMR spectrum of **1** after partial crystallisation. The **1**-*cis* isomer is less soluble and signals corresponding to it dominate in this spectrum. The presence of two independent sets of signals reveal rigid behaviour of **1**-*cis* and **1**-*trans* in solution. The ^{1}H-NMR patterns of both isomers are similar in the –CH and –CH$_3$ regions and consist of one and three singlets, respectively. Substantial differences are observed in the Al–CH$_3$ groups region of the spectrum, which results from the different geometry of these compounds. The five singlets of equal intensity correspond to **1**-*cis*; in the latter all Al–CH$_3$ groups are
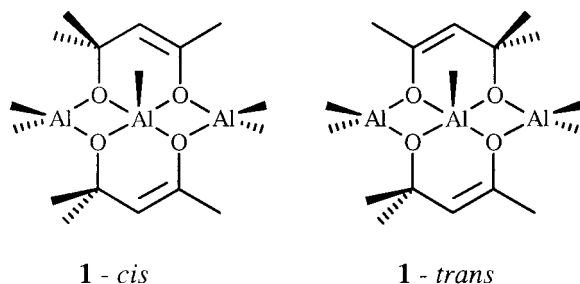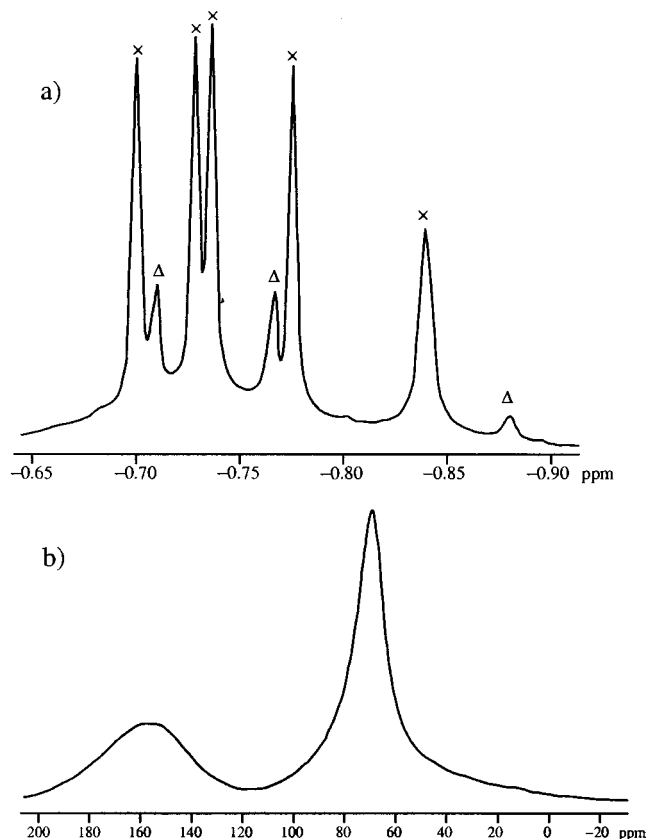

Fig. 1. (a) ^{1}H-NMR spectrum of [MeAl][C$_{12}$H$_{20}$O$_4$][AlMe$_2$]$_2$ (**1**) in the Al–CH$_3$ protons region after partial crystallisation; the assignments of the signals of **1**-*cis* and **1**-*trans* isomers are denoted by cross and triangle, respectively. (b) ^{27}Al-NMR spectrum of **1**.

non-equivalent. For **1**-*trans* three singlets of 2:2:1 intensity are observed since the methyl groups in dimethylaluminium species are related by symmetry in pairs. The ^{27}Al-NMR spectrum (Fig. 1b) shows two resonances at 154 and 68 ppm: the higher field resonance correspond to four-coordinated dialkylaluminium alkoxide adducts [7] and the lower field resonance is consistent with a five-coordinated aluminium atom in CAlO$_4$ environment, i.e. in MeAl(mesal)$_2$ where mesal = methyl salicylate anion ([5]a).

The structure of **1**-*cis* was confirmed by X-ray crystallography. The molecular structure of **1**-*cis* is shown in Fig. 2 and selected bond lengths and angles are given in Tables 1 and 2, respectively. The compound has a quasi C$_s$ symmetry with the symmetry plane through three aluminium atoms. The central Al(1) aluminium atom is five-coordinated, residing in a square pyramidal geometry with the basal plane consisting of four oxygen atoms of the acac-Me moieties and the methyl group residing in an apical position. The four oxygen atoms deviate only slightly from the least-square basal plane-the highest deviation is equal 0.017(1) Å. The aluminium atom is displaced 0.652(1) Å from the O$_4$ basal plane. The coordination sphere geometry of the central
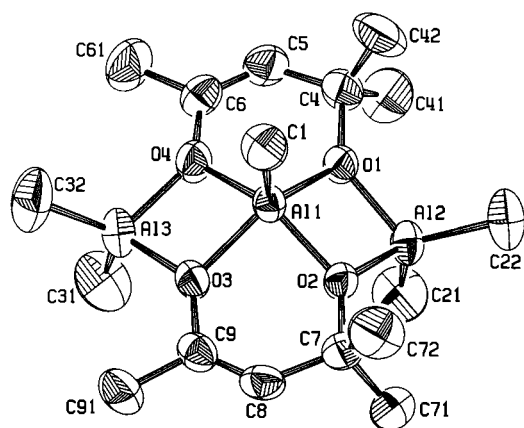

1 - *cis*   **1** - *trans*

Scheme 1.

Fig. 2. ORTEP diagram of [MeAl][$C_{12}H_{20}O_4$][AlMe$_2$]$_2$ (**1**-*cis*) showing a 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

aluminium atom in **1**-*cis* is essentially the same as that observed for related trinuclear aluminium complex derived from the glycolate dianion, [RAl][(OCH$_2$CH$_2$O)$_2$][AlR$_2$]$_2$, where R = CH(SiMe$_3$)$_2$ [8]. The carbon atoms of the heterocyclic AlOCCCO ring lies almost in a basal plane defined by oxygen atoms, and the six-membered AlOCCCO ring has a form of an opened envelope. The four *cis* OAlO angles range from 75.9 to 88.9°, the *trans* OAlO angles are 138.1(1) and 140.2(1)°. The Al(1)–O bond distances range from 1.846(2) to 1.892(2) Å. The bonds to the enolate oxygen atoms are significantly longer (average Al–O$_{enolate}$ = 1.892 Å and Al–O$_{alkoxide}$ = 1.849 Å) which results from the lower basicity of the enolate oxygen in comparison to the alkoxide oxygen. The mean Al(1)–O bond distance, 1.870 Å, is equal to the corresponding value observed by us in a simple monomeric five-coordinated organoaluminium complex, MeAl(mesal)$_2$ ([5]a), with a bipyramidal CAlO$_4$ core: Al–O$_{eq}$ 1.773(2) Å, Al–O$_{ax}$ 1.968(1) Å. The Al(1)–C(1) bond distance, 1.945(3) Å, is similar to that observed for MeAl(mesal)$_2$ [1.941(5) Å]. This indicates that the Al–C bond is insensitive toward changes in the coordination geometry of five-coordinated complexes.

Table 1
Selected bond lengths [Å] for compound **1**-*cis*

Al(1)–O(2)	1.846(2)	Al(1)–O(1)	1.852(2)
Al(1)–O(4)	1.891(2)	Al(1)–O(3)	1.892(2)
Al(1)–C(1)	1.945(3)	Al(2)–O(1)	1.827(2)
Al(2)–O(2)	1.832(2)	Al(2)–C(21)	1.931(4)
Al(2)–C(22)	1.937(4)	Al(3)–O(4)	1.834(2)
Al(3)–O(3)	1.835(2)	Al(3)–C(31)	1.942(4)
Al(3)–C(32)	1.945(4)	O(1)–C(4)	1.452(4)
O(2)–C(7)	1.441(4)	O(3)–C(9)	1.376(4)
O(4)–C(6)	1.378(4)	C(4)–C(5)	1.485(5)
C(5)–C(6)	1.313(4)	C(7)–C(8)	1.502(4)
C(8)–C(9)	1.304(4)		

Table 2
Selected bond angles [°] for compound **1**-*cis*

O(1)–Al(1)–O(4)	88.78(9)	O(2)–Al(1)–O(3)	88.89(9)
O(2)–Al(1)–O(4)	140.21(10)	O(1)–Al(1)–O(3)	138.05(10)
O(1)–Al(1)–O(2)	78.36(9)	O(3)–Al(1)–O(4)	75.86(9)
O(2)–Al(1)–C(1)	112.88(13)	O(1)–Al(1)–C(1)	113.05(13)
O(4)–Al(1)–C(1)	106.82(13)	O(3)–Al(1)–C(1)	108.75(12)
O(1)–Al(2)–O(2)	79.35(9)	O(1)–Al(2)–C(21)	111.7(2)
O(2)–Al(2)–C(21)	112.3(2)	O(1)–Al(2)–C(22)	113.8(2)
O(2)–Al(2)–C(22)	113.14(14)	O(3)–Al(3)–O(4)	78.66(9)
O(4)–Al(3)–C(31)	112.4(2)	O(3)–Al(3)–C(31)	112.9(2)
O(4)–Al(3)–C(32)	113.2(2)	O(3)–Al(3)–C(32)	112.6(2)
Al(2)–O(1)–Al(1)	101.05(10)	Al(2)–O(2)–Al(1)	101.08(10)
Al(3)–O(3)–Al(1)	102.56(11)	Al(3)–O(4)–Al(1)	102.58(11)

The terminal aluminium atoms are bonded to two alkoxide oxygen atoms, O(1) and O(2), or to two enolate oxygen atoms, O(3) and O(4). Although terminal Al(2) and Al(3) aluminium atoms are bonded to different pairs of oxygen centres, all Al(2)–O and Al(3)–O bond distances are very similar (range from 1.827(2) to 1.835(2) Å). The observed equalisation of Al–O bonds to the four-coordinated Al atoms shows that the central five-coordinated Al atom in Me$_2$Al-μ-(O)$_2$AlMe-μ-(O)$_2$AlMe$_2$ system (a weaker Lewis acid centre) act like a buffer between two four-coordinated dialkylaluminium moieties (very strong Lewis acid centres).

It is interesting to note that fully structurally characterised trinuclear compounds similar to complex **1** have been obtained from reactions of aluminium alkyls with diols [8,9], amino alcohols [10], alkyldiamine [11] or Schiff base type ligands [12], i.e. trimetallic derivatives of the general formula RAl[(dianion)AlR$_2$]$_2$.

The results reported show how knowledge about the structure of intermediate compounds is helpful in understanding of the role played by the molar ratio of reactants. In the reaction of Me$_3$Al with monofunctional ketones a drastic decrease in the reaction rate was observed [12], while in the alkylation of the carbonyl group in the chelated acetylacetonate ligand we observed an increase in the reaction rate in time. These variations in the reaction rate are due to the different structures of organoaluminium intermediates derived from the alkylation of carbonyl groups in monofunctional ketones and bifunctional carbonyl compounds (Scheme 2). The initial step in both reactions is undoubtedly the formation of the corresponding Lewis acid–base adduct [6,13,14]. A decrease in the reaction rate for monofunctional ketones is consistent with the 'consumption' of an alkylating reagent by the simple alkoxide compound formed, contrary to the latter, where the formation of trinuclear compound **1** relieves a Me$_3$Al molecule.

Further studies on the reactivity of bifunctional carbonyl compounds towards organometallic reagents are in progress in our laboratory.

Scheme 2.
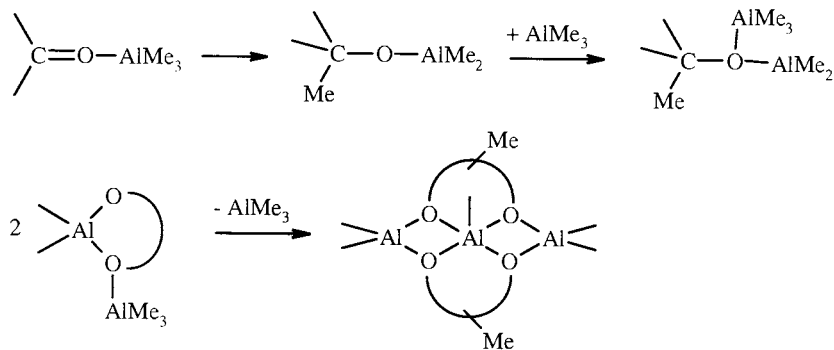
3. Experimental details

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 using standard Schlenk line techniques. Solvents were purified and dried by standard techniques. Trimethylaluminium was distilled before use. NMR spectra were recorded on a Varian VXR-300 spectrometer.

3.1. Reactions of $Me_2Al(acac)$ with $AlMe_3$

To a toluene solution (12 cm^3) of $Me_2Al(acac)$ (1.25 g, 8.0 mmol) $AlMe_3$ was added (0.58 g, 8.0 mmol,) at r.t. via a syringe. After stirring for an additional period of 1 h at 30°C, the solution was evaporated to dryness in vacuo to leave a white solid. This solid was identified on the basis of ^{1}H-NMR spectra as an equimolar mixture of cis-/trans-**1**. Both isomers were separated by fractional crystallisation from hexane. The solution of the crude product in hexane was stored overnight at −15°C. Then precipitate was separated by decanting and after recrystallisation from hexane/toluene mixture it was identified as the **1**-cis isomer. The solution poured off was evaporated in vacuo to dryness and the obtained solid was identified as **1**-trans. ^{1}H-NMR (CD$_2$Cl$_2$, 20°C): **1**-trans, $\delta = -0.88$ (s, 3H, Al(CH$_3$); −0.76 (s, 6H, Al(CH$_3$)$_2$); −0.70 (s, 6H, Al(CH$_3$)); 1.37 (s, 6H, C–CH$_3$); 1.41 (s, 6H, C–CH$_3$); 1.77 (s, 6H, C–CH$_3$); 4.37 (s, 2H, CH); ^{27}Al-NMR, $\delta = 65$ ($\Delta H_{\frac{1}{2}} = 1150$ Hz), 155 ($\Delta H_{\frac{1}{2}} = 4140$ Hz). **1**-cis, $\delta = -0.84$ (s, 3H, Al(CH$_3$)); −0.77 (s, 3H, Al(CH$_3$)$_2$); −0.73 (s, 3H, Al(CH$_3$)$_2$); −0.72 (s, 3H, Al(CH$_3$)$_2$); −0.69 (s, 3H, Al(CH$_3$)$_2$); 1.35 (s, 3H, C–CH$_3$); 1.39 (s, 6H, C–CH$_3$); 1.82 (s, 6H, C–CH$_3$); 4.37 (s, 2H, CH); ^{27}Al-NMR, $\delta = 66$ ($\Delta H_{\frac{1}{2}} = 1090$ Hz), 158 ($\Delta H_{\frac{1}{2}} = 4150$ Hz). Anal. found for **1**: C, 53.2; H, 9.1; Al, 21.0. C$_{17}$H$_{35}$Al$_3$O$_4$ calc.: C, 53.12; H, 9.18; Al, 21.06. The rate of the alkylation reactions for different molar ratios of reactants in C$_6$D$_6$ at 30°C were determined by the analysis of ^{1}H-NMR spectra acquired during reaction in a NMR tube.

3.2. X-ray structure determination

A selected crystal of **1**-cis was placed in a thin walled capillary tube (Lindemann glass) in an inert atmosphere. The tube was plugged with grease, then flame-sealed and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. Crystal data and details of data collection and refinement procedure are presented in Table 3. The orientation matrix was obtained from the least-squares refinement of the

Table 3
Crystallographic data and details of data collection and structure refinement for compound **1**-cis

Empirical formula	C$_{17}$H$_{35}$Al$_3$O$_4$
Formula weight	384.40
Temperature (K)	293(2)
Wavelength (Å)	0.71073 (Mo–K$_\alpha$)
Crystal system	Triclinic
Space group	P$\bar{1}$
Unit cell dimensions	
a (Å)	10.595(2)
b (Å)	10.818(2)
c (Å)	12.194(2)
α (°)	74.303(13)
β (°)	86.70(2)
γ (°)	61.317(14)
V (Å^3)	1176.2(4)
Z	2
D_{calc} (g cm^{-3})	1.085
μ (mm^{-1})	0.176
$F(000)$	416
θ range for data collection (°)	2.2–25.0
h_{min}, h_{max}	0, 9
k_{min}, k_{max}	−11, 12
l_{min}, l_{max}	−14, 14
Reflections collected	3868
Independent reflections	3636
R_{int}	0.0169
Data/restraints/parameters	3635/0/258
Goodness-of-fit on F^2	1.003
R_1 [$I > 2\sigma(I)$]	0.0442
wR_2 [$I > 2\sigma(I)$]	0.0990
R_1 (all data)	0.0834
wR_2 (all data)	0.1148
Largest difference peak and hole (e Å^{-3})	+0.20 and −0.23

Table 4
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^{-3}$ Å^{-2}) for compound **1**-*cis*

Atom	x	y	z	U_{eq}
Al(1)	1711(1)	6602(1)	6873(1)	41(1)
Al(2)	473(1)	8029(1)	8606(1)	50(1)
Al(3)	3339(1)	3467(1)	7126(1)	57(1)
O(1)	2145(2)	7362(2)	7897(2)	47(1)
O(2)	−5(2)	7375(2)	7541(2)	44(1)
O(3)	1471(2)	4967(2)	6913(2)	49(1)
O(4)	3604(2)	4995(2)	7211(2)	55(1)
C(1)	1573(4)	7688(4)	5286(3)	65(1)
C(21)	712(5)	6799(5)	10142(3)	94(1)
C(22)	−582(5)	10142(4)	8308(4)	85(1)
C(31)	3768(5)	2009(5)	8593(4)	103(2)
C(32)	4004(5)	2850(5)	5748(4)	96(1)
C(4)	3440(4)	7477(4)	8002(3)	61(1)
C(41)	3610(5)	7547(6)	9215(4)	96(2)
C(42)	3250(5)	8873(4)	7118(4)	91(1)
C(5)	4720(4)	6159(4)	7816(3)	65(1)
C(6)	4809(3)	5071(4)	7474(3)	58(1)
C(61)	6178(4)	3809(5)	7322(5)	94(1)
C(7)	−1349(3)	7468(3)	7238(3)	54(1)
C(71)	−2253(4)	7630(5)	8263(4)	82(1)
C(72)	−2123(4)	8805(4)	6217(4)	86(1)
C(8)	−1052(4)	6096(4)	6947(3)	55(1)
C(9)	166(4)	5000(3)	6822(2)	50(1)
C(91)	308(5)	3660(4)	6563(4)	77(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

angular positions measured for 25 reflections in the 2θ range between 6 and 25°. The intensities were collected up to $2\theta = 50°$ in the $\omega - 2\theta$ mode. Two check reflections repeated every 70 reflections showed a 14% decrease of net intensity. After correction for the Lorentz-polarization effect and crystal decomposition, the equivalent reflections were averaged. The resulting 3636 unique reflections had the internal consistency index $R_{int} = 0.0169$. The phase problem was solved in the P$\bar{1}$ space group by direct methods using the SHELXS86 program [15]. The structure was refined on F^2 by full-matrix least-squares methods (SHELXL93 program [16]) with isotropic thermal parameters in the first step. After full convergence of the isotropic refinement, anisotropic thermal parameters were assigned for all non-H atoms. Although some of the H atoms could be found in subsequent difference Fourier maps, all were set riding in calculated positions with isotropic thermal parameters. Hydrogen atoms of all methyl groups bonded to Al atoms were refined as disordered groups with two positions rotated 60° about the C–Al bond. In the final stages of refinement, data were weighted according to $w^{-1} = [\sigma^2(F_o^2) + (0.0570P)^2 + 0.1294P]$, where $P = (F_o^2 + 2F_c^2)/3$. The largest positive and negative peaks on final difference Fourier maps have no significant chemical meaning, and the maximum shift/error ratios

in final cycles of refinement were < 0.001. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4. Tables of anisotropic thermal parameters, hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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