Synthesis and Characterisation of Manganese(II) Chalcogenolato Complexes. Crystal and Molecular Structure of $[\{Mn(\mu\text{-}SeC_6H_2Me_3\text{-}2,4,6)_2\}_\infty]$†

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A series of manganese(II) complexes $[\{Mn(EC_6H_2R'_3\text{-}2,4,6)_2\}]$ (E = Se, R' = Me or Bu^t; E = Te, R' = Me) have been prepared by protolysis of $[Mn\{N(SiMe_3)_2\}_2(thf)]$ (thf = tetrahydrofuran) with the corresponding sterically demanding arenechalcogenols $2,4,6\text{-}R'_3C_6H_2EH$. Complexes with R' = Me form co-ordination polymers which are soluble only in strongly co-ordinating solvents, while complexes with R' = Bu^t are dimeric and readily dissolve in less polar solvents such as toluene. The complexes react with Lewis bases (PMe_3, 2,2'-bipyridyl) to form tetrahedral or octahedral adducts, depending on the steric requirements of the arenechalcogenolate ligands. The structure of $[\{Mn(\mu\text{-}SeC_6H_2Me_3\text{-}2,4,6)_2\}_\infty]$ was determined by X-ray diffraction. The compound forms a one-dimensional infinite chain with bridging selenolate ligands which surround the metal centre in a flattened tetrahedral geometry.

Metal chalcogen complexes have attracted significant attention in recent years because of their rich structural chemistry and potential applications in materials chemistry.[1] One such application is their use as starting materials for the synthesis of semiconductors, including the deposition of chalcogenide films from the gas phase.[2–4] As part of our search for volatile metal chalcogenolato Group 12 complexes as single-source precursors for II–VI semiconductor materials we have recently demonstrated that sterically hindered thiolato and selenolato complexes of zinc and cadmium can form monomers and dimers[5,6] which are sufficiently volatile to allow the deposition of metal chalcogenide films from the gas phase by low-pressure metal–organic chemical vapour deposition (MOCVD) methods.[3] While interest so far has largely centred on complexes of zinc, cadmium and mercury, other metals are now beginning to attract attention. Some dimeric thiolato complexes of manganese(II), iron(II) and cobalt(II) have recently been reported.[7] Manganese plays a role as a dopant for II–VI semiconductor films and as a source of magnetic semiconductors.[8] We report here the synthesis and characterisation of new manganese(II) selenolato and tellurolato complexes.

Results and Discussion

The protolysis of $[Mn\{N(SiMe_3)_2\}_2(thf)]$ (thf = tetrahydrofuran) with arenechalcogenols $2,4,6\text{-}R'_3C_6H_2EH$ (E = Se, R' = Me or Bu^t; E = Te, R' = Me) in non-co-ordinating solvents, preferably light petroleum, provides a convenient route to the corresponding chalcogenolato **1**–**3** complexes in high yield as shown in Scheme 1.

Mesityl Complexes.—The reaction of R^1EH (R^1 = $2,4,6\text{-}Me_3C_6H_2$, E = Se or Te) with $[Mn\{N(SiMe_3)_2\}_2(thf)]$ according to Scheme 1 leads to the immediate precipitation of $Mn(SeR^1)_2$ **1** and $Mn(TeR^1)_2$ **2**. The compounds are highly air-sensitive and dissolve only in co-ordinating solvents such as dimethylformamide (dmf), thf or pyridine; **1** can be recrystallised from thf–light petroleum to give pale pink cubes while the attempted recrystallisation of **2** leads to decomposition and formation of dimesityl ditelluride. As expected for polymeric complexes with bridging chalcogenolato ligands, compounds **1** and **2** do not sublime. Both decompose above 220 °C.

$$[Mn\{N(SiMe_3)_2\}_2(thf)] + 2R'_3C_6H_2EH \longrightarrow Mn(EC_6H_2R'_3)_2 + 2NH(SiMe_3)_2 + thf$$

Scheme 1 E = Se, R = Me **1** or Bu^t **3**; E = Te, R = Me **2**

In the presence of an excess of 2,2'-bipyridyl (bipy) compound **1** reacts to give the 1:2 adduct $[Mn(SeR^1)_2(bipy)_2]$ **1a**. In contrast to related chalcogenolato complexes of Zn^{II} which form four-co-ordinate adducts with bipy,[9] manganese(II) is evidently able to increase its co-ordination sphere to give octahedral adducts. Complex **2** reacts with bipy in an analogous fashion to give a brown microcrystalline product of stoichiometry $Mn_2(TeR^1)_4(bipy)_3$ **2a**. Both **1a** and **2a** are significantly more soluble than **1** or **2** but are not volatile. Although several other nitrogen- and phosphorus-donor ligands such as 2,6-dimethylpyridine, *tert*-butyl isocyanide, PMe_3 and $Me_2PCH_2CH_2PMe_2$ (dmpe) were allowed to react with **2** in an effort to obtain crystals suitable for a structure determination, the products lacked crystallinity and could not be adequately purified.

*Tri-*tert*-butylphenyl Complexes.*—Following Scheme 1, $Mn(SeR^2)_2$ **3** (R^2 = $2,4,6\text{-}Bu^t_3C_6H_2$) is obtained by the addition of R^2SeH to $[Mn\{N(SiMe_3)_2\}_2(thf)]$ at low temperature as a pale pink microcrystalline solid which darkens rapidly on exposure to traces of air. As was shown previously for related complexes of divalent metals such as Zn, Cd[2,5] and the thiolato analogue of **3**, $[\{Mn(SR^2)_2\}_2]$,[7] the high steric hindrance provided by the *o*-Bu^t substituents severely restricts the maximum co-ordination number the metal can obtain and leads to dimeric compounds with trigonal-planar metal centres. It is therefore likely that **3** possesses a similar dimeric structure, with two bridging and two terminal SeR^2 ligands.

Complex **3** reacts with PMe_3 to give the 1:2 adduct $[Mn(SeR^2)_2(PMe_3)_2]$ **3a**, while chelating ligands such as dmpe and bipy give $[Mn(SeR^2)_2(dmpe)]$ **3b** and $[Mn(SeR^2)_2(bipy)]$ **3c**, respectively. Octahedral complexes of stoichiometry

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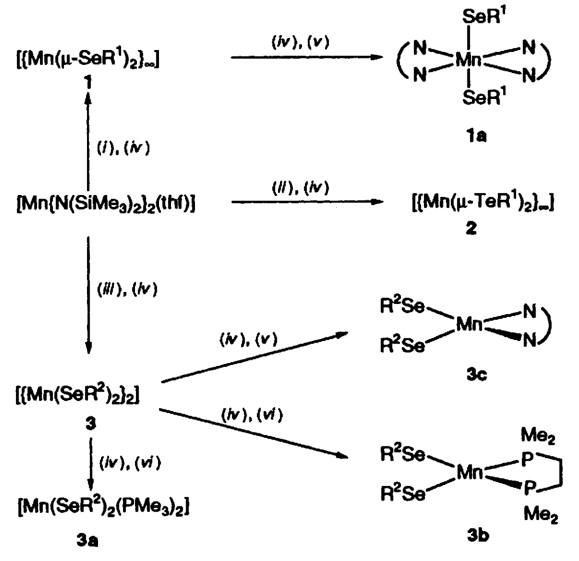
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$Mn(SeR^2)_2(bipy)_2$ can evidently not be formed even in the presence of an excess of bipy due to steric hindrance. Once again the adducts show increased solubility in solvents such as toluene; they also show a higher volatility and are therefore of interest as potential precursors to manganese selenide. The reactions are summarised in Scheme 2.

Infrared Spectra.—The Fourier-transform low-frequency infrared spectra in the region relevant to metal–ligand vibrations (150–500 cm^{-1}) have been recorded and are given in Table 1. The IR bands associated with metal–chalcogen stretching modes are readily identified. As expected for polymeric complexes with bridging chalcogenolate ligands, the M–E stretching modes of **1** and **2** contain a significant bending component and occur as rather broad bands at lower frequencies (< 250 cm^{-1}) than that of **3**. The ν(M–E) vibrations of the mononuclear bipyridyl and phosphine adducts are observed at wavenumbers *ca.* 20 cm^{-1} higher than those of **1–3**.

Crystal Structure of $Mn(SeR^1)_2$ **1**.—Since there are very few structurally characterised manganese chalcogenolato complexes the structure of **1** was determined by X-ray diffraction. The MnX_4 unit and the atomic numbering scheme are shown in Fig. 1, the chain structure and the mutual orientations of the chains in Fig. 2. Important bond lengths and angles are collected in Table 2, and positional parameters are in Table 3. The complex exists in the solid state as a one-dimensional infinite chain, with symmetrically bridging selenolate ligands. The Mn–Se bond distances of 2.590(3) Å are slightly longer than the terminal Mn–Se distances in the recently reported anion $[Mn(SePh)_4]^{2-}$ (average 2.567 Å).[10] The Mn_2Se_2 rings are planar, with the Mn(1)–Se(1)–Mn(1A) angles [88.0(1)°] being slightly more acute than the Se(1)–Mn(1)–Se(1A) angles [92.0(1)°], while the extraannular Se(1A)–Mn(1)–Se(1B) angles are very much wider, 118.8(1)°. As a result the co-ordination geometry around Mn consists of a flattened tetrahedron. The selenium atoms are pyramidal (angle sum 314.8°), and the mesityl groups are oriented around the chain so as to minimise steric interactions. The extent of aggregation of arenechalcogenolato complexes of divalent metals has been shown to be sensitive to the steric requirements of *ortho*-substituents on the phenyl ring, and three- and two-dimensional networks exist.[11] The structure of **1** is strongly reminiscent of that of $[\{Cd(\mu\text{-}TeR^1)_2\}_\infty]$[12] and it is probable that **2** also exists as a one-dimensional chain. By contrast, the recently reported amidoselenolato complex $[\{Mn[N(SiMe_3)_2](SeC_6H_2Pr^i{}_3\text{-}2,4,6)(thf)\}_2]$ retains one solvent molecule per metal centre and forms a selenolato-bridged dimer.[13]



Scheme 2 (*i*) 2,4,6-$Me_3C_6H_2SeH$ (R^1SeH); (*ii*) 2,4,6-$Me_3C_6H_2TeH$ (R^1TeH); (*iii*) 2,4,6-$Bu^t{}_3C_6H_2SeH$ (R^2SeH); (*iv*) light petroleum, room temperature; (*v*) 2,2′-bipyridyl, thf; (*vi*) excess of trialkylphosphine

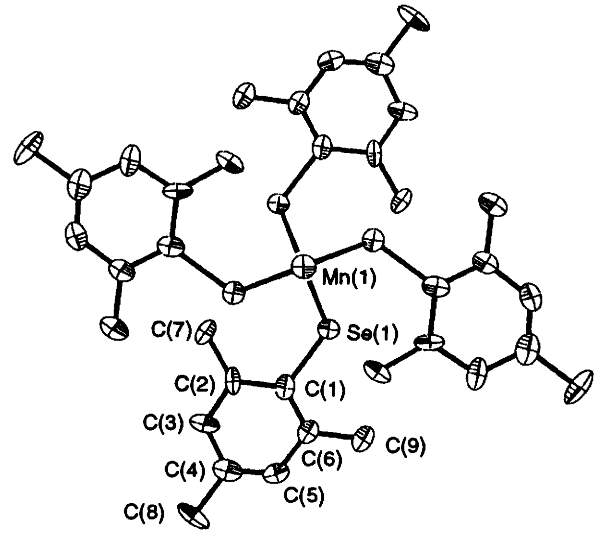


Fig. 1 View of a $Mn(\mu\text{-}SeC_6H_2Me_3)_4$ unit of complex **1** showing the atomic numbering scheme. Ellipsoids correspond to 30% probability

Experimental

General Procedures.—All reactions were carried out under inert gas using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium–benzophenone [diethyl ether, thf, light petroleum (b.p. 40–60 °C)], sodium (toluene, heptane) or calcium hydride (dichloromethane). The NMR solvents were stored over 4A molecular sieves under nitrogen or argon and degassed by several freeze–thaw cycles. The compounds 2,4,6-$Me_3C_6H_2SeH$ (R^1SeH),[5a] 2,4,6-$Me_3C_6H_2$-TeH (R^1TeH),[12] 2,4,6-$Bu^t{}_3C_6H_2SeH$ (R^2SeH)[2] and $[Mn\{N(SiMe_3)_2\}_2(thf)]$[14] were prepared as descibed. Melting points are uncorrected. Infrared spectra were recorded on Mattson Polaris, Nicolet F20 and Perkin-Elmer 684 spectrometers, NMR spectra on a JEOL EX270 instrument. Magnetic

Table 1 Low-frequency infrared spectroscopic data for manganese chalcogenolato complexes *

$Mn(SeR^1)_2$	$[Mn(SeR^1)_2(bipy)_2]$	$Mn(TeR^1)_2$	$Mn_2(TeR^1)_4(bipy)_3$	$Mn(SeR^2)_2$	$[Mn(SeR^2)_2(PMe_3)_2]$	$[Mn(SeR^2)_2(bipy)]$
1	**1a**	**2**	**2a**	**3**	**3a**	**3c**
452s	413m	456s	476s (br)	479w	480w	480 (br)
	407 (sh)		412s	440w	440w	414m
345w	348w	352s	390s (br)	387m	360m (br)	356w (br)
	327w					
259w	253w	259m	227s ν(Mn–Te)	271 ν(Mn–Se)	259 ν(Mn–Se)	262 ν(Mn–Se)
211s ν(Mn–Se)	229s ν(Mn–Se)	201s (br)		218 (br)	212 (br)	
199m (sh)	189s	ν(Mn–Te)	189m			
	178s		176m			

* Nujol mulls, polyethylene plates.

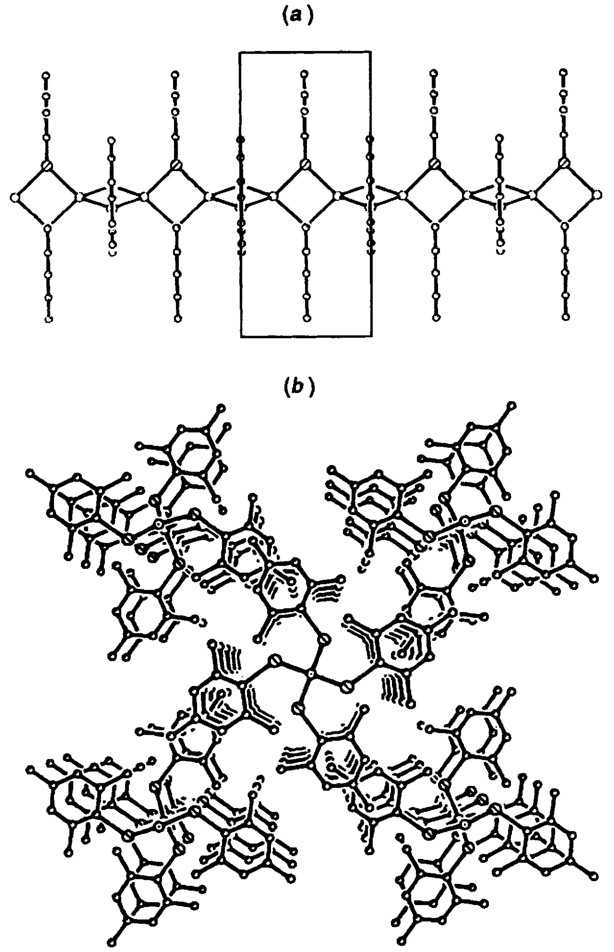


Fig. 2 Side view of one chain of [{Mn(μ-$SeC_6H_2Me_3$-2,4,6)$_2$}$_\infty$] **1** (*a*) and a view down the *c* axis showing the packing arrangement of the individual chains in the crystal (*b*)

Table 2 Selected bond lengths (Å) and Angles (°) of compound **1**

Se(1)–Mn(1)	2.590(3)	Se(1)–C(1)	1.963(19)
C(1)–C(2)	1.421(24)	C(1)–C(6)	1.379(26)
C(2)–C(3)	1.411(27)	C(2)–C(7)	1.496(27)
C(3)–C(4)	1.406(27)	C(4)–C(5)	1.316(29)
C(4)–C(8)	1.570(30)	C(5)–C(6)	1.429(26)
C(6)–C(9)	1.490(27)		
Mn(1)–Se(1)–C(1)	112.1(4)	Mn(1)–Se(1)–Mn(1A)	88.0(1)
C(1)–Se(1)–Mn(1A)	112.1(4)	Se(1)–Mn(1)–Se(1A)	92.0(1)
Se(1)–Mn(1)–Se(1B)	118.8(1)	Se(1)–C(1)–C(2)	120.3(14)
Se(1)–C(1)–C(6)	116.1(13)		

Table 3 Atomic coordinates (10^4) of compound **1**

Atom	*x*	*y*	*z*
Se(1)	1104(1)	413(1)	0
Mn(1)	0	0	2500
C(1)	2084(12)	−350(12)	0
C(2)	1965(13)	−1241(10)	0
C(3)	2705(11)	−1741(14)	0
C(4)	3510(12)	−1363(13)	0
C(5)	3574(11)	−533(12)	0
C(6)	2868(11)	33(12)	0
C(7)	1133(12)	−1693(12)	0
C(8)	4302(14)	−1964(15)	0
C(9)	3000(14)	966(12)	0

moments of the solids were measured at room temperature using a Johnson Matthey magnetic balance. Elemental analyses and physical properties are collected in Table 4.

Syntheses.—Mn(SeR^1)$_2$ **1**. To a solution of R^1SeH (1.24 g, 6.26 mmol) in light petroleum (30 cm^3) was added [Mn{N($SiMe_3$)$_2$}$_2$(thf)] (1.40 g, 3.13 mmol) at room temperature. A pale precipitate formed immediately. The mixture was stirred for 2 h and filtered. The solid was washed with light petroleum and dried *in vacuo* to give compound **1** (1.25 g, 88.5%). The product can be recrystallised from thf–light petroleum (4:1 v/v) to give pale pink cubic crystals.

[Mn(SeR^1)$_2$(bipy)$_2$] **1a**. 2,2′-Bipyridyl (0.518 g, 3.32 mmol) was added to Mn(SeR^1)$_2$ (0.554 g, 1.23 mmol) suspended in light petroleum (20 cm^3) at room temperature. Dissolution of Mn(SeR^1)$_2$ followed by precipitation of the product was observed. The mixture was stirred for 1.5 h and filtered. The residue was recrystallised from thf at −16 °C to give the product as a dark brown microcrystalline solid (0.85 g, 91%).

Mn(TeR^1)$_2$ **2**. This complex was made as described for compound **1**, with the exception that R^1TeH was generated below −30 °C and added to [Mn{N($SiMe_3$)$_2$}$_2$(thf)] at −78 °C. The mixture was then allowed to warm slowly to room temperature to give a pale pink solid (95%).

Mn_2(TeR^1)$_4$(bipy)$_3$ **2a**. 2,2′-Bipyridyl (0.387 g, 2.48 mmol) was added to Mn(TeR^1)$_2$ (0.349 g, 0.64 mmol) dissolved in thf (20 cm^3) at room temperature. The mixture was stirred for 1 h, the solvent removed *in vacuo* and the residue washed with light petroleum. After recrystallisation from thf at −16 °C the product was obtained as a dark brown microcrystalline solid (0.49 g, 89%).

Mn(SeR^2)$_2$ **3**. The compound [Mn{N($SiMe_3$)$_2$}$_2$(thf)] (0.69 g, 1.55 mmol) in light petroleum (6 cm^3) was added to a solution of R^2SeH (1.0 g, 3.10 mmol) in light petroleum (30 cm^3) at −78 °C. A white precipitate formed over the next 10 min. The mixture was allowed to warm to room temperature and stirred for 1 h. The solid was filtered off, washed with light petroleum and dried *in vacuo* to give compound **3** (1.06 g, 98%). Recrystallisation from toluene gave a fine crystalline pale pink solid.

[Mn(SeR^2)$_2$(PMe_3)$_2$] **3a**. The compound Mn(SeR^2)$_2$ (0.50 g, 0.71 mmol) suspended in light petroleum (10 cm^3) was treated with PMe_3 (0.42 cm^3, 2.13 mmol) at room temperature. After stirring the mixture for 1 h the solvent was removed and the residue recrystallised from a mixture of dichloromethane and light petroleum at −16 °C to give the product as yellow microcrystals (0.53 g, 87%).

[Mn(SeR^2)$_2$(dmpe)] **3b**. In a method analogous to that for **3a**, compound **3b** was prepared from Mn(SeR^2)$_2$ (0.33 g, 0.47 mmol) and dmpe (0.80 mmol) as a pale yellow solid (0.37 g, 91%).

[Mn(SeR^2)$_2$(bipy)] **3c**. 2,2′-Bipyridyl (0.52 g, 3.33 mmol) was added to Mn(SeR^2)$_2$ (0.81 g, 1.15 mmol) suspended in light petroleum (20 cm^3) at room temperature. The mixture was stirred for 1 h and the solvent removed *in vacuo*. The residue was recrystallised from thf–light petroleum (4:1 v/v) at −16 °C to give the product as a dark pink microcrystalline solid (0.91 g, 92%). On heating the compound to its melting point in a sealed class tube ligand dissociation took place and free bipy sublimed.

X-Ray Crystallography.—Crystals of compound **1** were grown from thf–light petroleum (4:1 v/v) at room temperature as pink cubes. X-Ray measurements were made using a crystal of dimensions 0.25 × 0.27 × 0.30 mm mounted in a sealed capillary tube under argon.

Crystal data. $C_{18}H_{22}MnSe_2$, M = 451.2, tetragonal, space group $P4_2/mbc$, a = 15.802(9), c = 7.195(7) Å, U = 1797(2) Å^3, Z = 4, D_c = 1.667 g cm^{-3}, μ(Mo-Kα) = 4.344 mm^{-1}, F(000) = 804.

Data collection. Data were collected at room temperature on

Table 4 Physical and analytical data

Compound		Colour	M.p./°C	μ/μ_B[a]	Analysis (%)[b]		
					C	H	N
1	$Mn(SeR^1)_2$	Pale pink	> 220	3.91	47.6 (47.9)	4.9 (4.9)	
1a	$[Mn(SeR^1)_2(bipy)_2]$	Dark brown	126 (decomp.)[c]	5.77	59.5 (59.8)	5.1 (5.0)	6.5 (7.3)
2	$Mn(TeR^1)_2$	Pale pink	> 220	5.28	36.8 (39.4)	3.9 (4.0)	
2a	$Mn_2(TeR^1)_4(bipy)_3$	Dark brown	> 110 (decomp.)[c]		50.8 (50.6)	4.5 (4.4)	5.5 (5.6)
3	$Mn(SeR^2)_2$	White	182	5.31	61.1 (61.5)	8.7 (8.3)	
3a	$[Mn(SeR^2)_2(PMe_3)_2]$	Pale yellow	156–158	5.42	58.7 (59.0)	9.0 (8.9)	
3b	$[Mn(SeR^2)_2(dmpe)]$	Pale yellow	138–140		58.2 (59.1)	8.7 (8.7)	
3c	$[Mn(SeR^2)_2(bipy)]$	Dark pink	126	5.49	63.5 (64.3)	7.7 (7.7)	3.1 (3.3)

[a] $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}. [b] Calculated values in parentheses. [c] With loss of 2, 2′-bipyridyl.

a Siemens R3m/V diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) and a graphite monochromator with ω scans in the range $2 \leqslant 2\theta \leqslant 50°$ with variable scan speeds (2.4–15.60° min^{-1} in ω) from $-18 < h < 0$, $-18 < k < 0$, $-8 < l < 0$. Of the 1869 reflections collected, 871 were independent with 571 considered as observed [$|F| > |4\sigma(F)|$]. A semiempirical absorption correction based on azimuthal Ψ scans was applied (maximum, minimum transmission = 0.130, 0.202).

Structure solution and refinement. The structure was solved by direct methods of phase determination using the SHELXTL (PLUS) package[15] and refined using successive cycles of full-matrix least squares; 63 parameters, data-to-parameter ratio 9.1 : 1, goodness of fit 0.96. Final R = 0.0681 and R' = 0.0947 where $w^{-1} = \sigma^2(F) + 0.0060F^2$; maximum and minimum electron densities were 1.42 and -1.12 e Å^{-3}, respectively. Hydrogen atoms were not included in the refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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