# Novel Manganese(II) Complexes formed from the Reaction of a Coarse-grain, Unactivated Manganese Powder with $PI_2(NMe_2)_3$ and $PI_2(C_6H_4SMe\text{-}o)_3$; Crystal Structure of the Dinuclear Complex $[\{MnI_2[P(NMe_2)_3]\}_2]$ †

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The reaction of $PI_2R_3$ (R = $NMe_2$ or $C_6H_4SMe$-*o*) with manganese metal powder has been studied. In agreement with previous studies, the nature of the products is highly dependent on R, and thus gives further evidence of the subtle nature of the reaction of diiodotriorganophosphorus compounds with metal powders. When R = $NMe_2$, the dinuclear complex $[\{MnI_2[P(NMe_2)_3]\}_2]$ is obtained, whereas when R = $C_6H_4SMe$-*o* a monomeric complex is obtained in which the phosphine acts as a chelating ligand. These results are in direct contrast to previously characterised phosphine complexes of this stoichiometry in which a polymeric complex is produced and which reversibly binds dioxygen. The complex $[\{MnI_2[P(NMe_2)_3]\}_2]$ has been crystallographically characterised and represents the first example of a dimeric species of this stoichiometry. Conductance and magnetic studies and the Raman spectrum of the complex $[MnI_2\{P(C_6H_4SMe\text{-}o)_3\}]$ indicate that a monomeric tetrahedral complex is produced in which the phosphorus and one sulfur atom chelate to the manganese centre.

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The existence of complexes of stoichiometry $MnI_2(PR_3)$ (R = aryl or alkyl) is well established, being first recognised in 1979.[1] Crystallographic characterisation of these compounds has revealed that two different isomers exist, *viz.* the polymeric structure exhibiting a chain of $MnI_2$ containing alternating tetrahedral ($MnI_4$) and pseudo-octahedral (*trans*-$MnI_4P_2$) units (the 4,6,4,6 structure)[2,3] and a further isomeric polymeric structure again exhibiting a chain of $MnI_2$ but which contains a single tertiary phosphine ligand bound syndiotactically to each manganese, thus creating a trigonal-bipyramidal geometry at the manganese centre (the 5,5,5,5 structure).[4] A feature of both types of complex is their ability to bind molecular oxygen at ambient temperatures and pressures.[5,6] The factors determining which isomer is favoured for any particular complex are not known with certainty, but may be related to their method of preparation.[6]

In addition to the complexes $[MnX_2(PR_3)]$ (X = halide, R = alkyl or aryl), several other manganese–phosphine complexes have been characterised crystallographically both by us and other workers. Thus, the mononuclear tetrahedral bis(phosphine) species, $[MnI_2(PR_3)_2]$ (R = Et[7] or Ph[6]), have been recognised as well as both a dinuclear[3] and trinuclear[8] species, these two being formed from the exposure of the polymeric $MnI_2(PR_3)$ complexes to trace levels of molecular oxygen. On the other hand Wilkinson and co-workers[9] have synthesised the dimeric species $[\{Mn(CH_2SiMe_3)_2(PMe_3)\}_2]$, which contains the manganese in tetrahedral geometry. However, no manganese–phosphine complexes of stoichiometry $MnI_2(PR_3)$ exhibiting a monomeric or dimeric structure has been previously described.

We have recently reported the novel reaction of dihalogenotriorganophosphorus compounds, $PX_2R_3$ (X = Br or I), with coarse grain metal powders to produce both transition-metal[3,4,6,10] and main-group metal[11] phosphine complexes. We have found that the reaction is subtle, being dependent on R and X.[6,10] In some cases the products derived from this new synthetic route are novel and are not easily available from known literature methods.[6,10]

Following our previous reports regarding the general reaction of $PX_2R_3$ with manganese powder to produce the polymeric complexes $MnX_2(PR_3)$ (X = Br or I; R = aryl or alkyl) and the monomeric complexes $[MnI_2(PR_3)_2]$ (R = Ph or substituted aryl),[3,4,6] we now report two manganese–phosphine complexes prepared by this synthetic route which exhibit unusual structures. Furthermore, we also show that the reaction of diiodotriorganophosphorus compounds, $PI_2R_3$, which contain substituted functional groups, with metal powders can lead to the isolation of complexes containing the tertiary phosphine as a chelating ligand. These results provide further evidence that the reaction of dihalogenotriorganophosphorus compounds with metal powders can produce unexpected and previously unknown products.

## Results and Discussion

Both of the complexes reported here are readily prepared from the direct reaction of the diiodotriorganophosphorus compound and manganese metal powder in diethyl ether under strictly anhydrous and anaerobic conditions [equation (1)].

$$PI_2R_3 + Mn \xrightarrow[Et_2O]{Ar,\ 5\ d} MnI_2(PR_3) \qquad (1)$$

|  | R |
|---|---|
| 1 | $NMe_2$ |
| 2 | $C_6H_4SMe$-*o* |

$[\{MnI_2[P(NMe_2)_3]\}_2]$ **1**.—Under the above experimental conditions complex **1**, with stoichiometry $MnI_2[P(NMe_2)_3]$, was isolated after approximately 5 d as a pale pink solid. Magnetic susceptibility measurements at room temperature give a magnetic moment value of 5.58, indicating a high-spin manganese(II) centre, with some antiferromagnetic coupling. Somewhat to our surprise, in contrast to almost all complexes of this stoichiometry, this complex showed no vivid colour change on exposure to molecular oxygen; the majority of $MnI_2(PR_3)$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

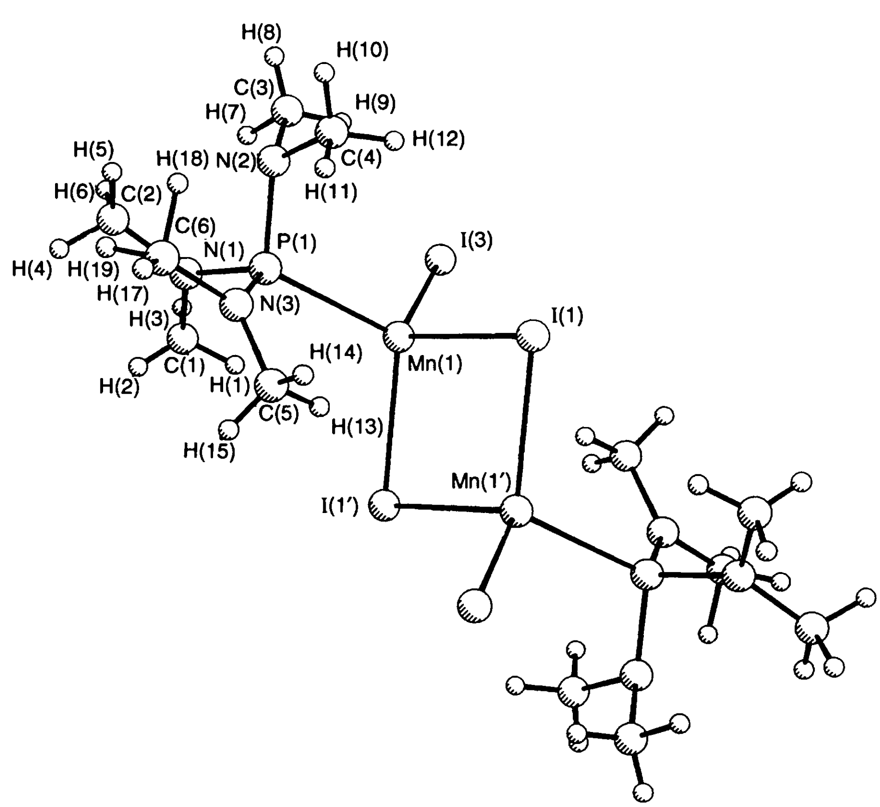

**Fig. 1** The crystal structure of the molecular dimer $[\{MnI_2[P(NMe_2)_3]\}_2]$

complexes react with $O_2$ to form the deep green $MnI_2(PR_3)(O_2)$ adducts.[1]

It occurred to us that this unusual unreactivity may be related to the structure of the complex, perhaps being different from the known polymeric $MnI_2(PR_3)$ complexes of identical stoichiometry. Consequently complex **1** was recrystallised from diethyl ether as pink block crystals. From these, one was selected and found to be suitable for single-crystal X-ray analysis. The structure of **1** is shown in Fig. 1. In contrast to the previously crystallographically characterised dioxygen-sensitive polymeric complexes of this stoichiometry, **1** exists as a discrete dinuclear species. The inability of this complex to bind molecular oxygen in either the solid state or in solution in common organic solvents may suggest that the polymeric nature of the $O_2$-binding complexes is intrinsically necessary for this function.

The dinuclear molecule of **1** (Fig. 1) lies on a crystallographic inversion centre; the bridging iodines have nearly identical Mn–I bond lengths [2.757(4) and 2.758(4) Å] these being similar to those exhibited by polymeric $MnI_2(PPhMe_2)$ [2.569(5)–2.902(5) Å][4] and $MnI_2(PMe_3)$ [2.707(3)–3.144(3) Å][3] (both structures contain a number of Mn–I bonds of different lengths). The terminal Mn–I distance of 2.618(3) Å is slightly shorter than the previously determined distances of 2.662(2), 2.670(2) and 2.670(6), 2.638(6) Å for the monomeric manganese(II) complexes, $[MnI_2(PEt_3)_2]$[7] and $[MnI_2(PPh_3)_2]$,[6] respectively. The Mn–P distance in **1**, 2.556(6) Å, is similar to all previously described manganese(II) complexes of tertiary phosphines, except for $[MnI_2(PPh_3)_2]$,[6] which exhibits atypically long Mn–P bonds [2.75(2) and 2.74(1) Å], probably due to steric factors at the more crowded monomeric manganese centre.

Although no manganese(II) complexes containing the $P(NMe_2)_3$ ligand have previously been described, the neutral iron carbonyl complex $[Fe(CO)_4\{P(NMe_2)_3\}]$[12] and, more recently, the planar $[PtCl_2\{P(NMe_2)_3\}_2]$[13] and the copper(I) species $[\{CuI[P(NMe_2)_3]\}_4]$,[14] containing a cubic $Cu_4I_4$ core, have been reported. In these three instances the complexes are typical of previously characterised iron(0), platinum(II) and copper(I) complexes containing tertiary phosphine ligands.[15] In vivid contrast then to previous behaviour, complex **1** containing this $P(NMe_2)_3$ ligand exhibits an unexpected structure, *viz.* dinuclear, $[(MnI_2L)_2]$, instead of polynuclear, $[(MnI_2L)_n]$. One reason for this may be steric; $P(NMe_2)_3$ has an extremely high cone angle of 157° [greater than $PPh_3$ (145°) and identical to that of the bulky ligand $PPh_2Bu^t$],[16,17] and the dinuclear structure may well relieve steric interactions present in the polymeric structures. Electronic factors may be important, though we cannot suggest why: the $pK_a$ of $P(NMe_2)_3$ is 7.58 (greater than $PPhMe_2$ at 6.49), and the 'electronic parameter' of $P(NMe_2)_3$, 2061.9 $cm^{-1}$, reported by Tolman,[17] is almost identical to that of $PEt_3$ (2061.7 $cm^{-1}$). Clearly, $P(NMe_2)_3$ is a bulky and basic ligand.

Our previous studies in this area have employed bulky ligands: $PPh_3$ forms the tetrahedral monomer $[MnI_2(PPh_3)_2]$, or non-sterically hindered rather basic phosphines such as $PMe_3$ which produces the acutely dioxygen-sensitive polymer $[\{MnI_2(PMe_3)\}_n]$. It can therefore be concluded that for the $P(NMe_2)_3$ ligand it is its steric bulk and high basicity, taken together, which results in the formation of the novel dinuclear structure $[\{MnI_2[P(NMe_2)_3]\}_2]$.

$[MnI_2\{P(C_6H_4SMe\text{-}o)_3\}]$.—The reaction of $PI_2(C_6H_4SMe\text{-}o)_3$ with manganese powder similarly produces a complex of 1 : 1 stoichiometry, $MnI_2[P(C_6H_4SMe\text{-}o)_3]$. This yellow complex **2**, like **1**, shows no ability to co-ordinate molecular oxygen either in the solid state or in solution in a range of common organic solvents.

Magnetic susceptibility measurements at room temperature give a magnetic moment value of 5.82, very close to the spin-only value expected for a magnetically dilute high-spin manganese(II) centre. Attempts to grow crystals suitable for single-crystal X-ray diffraction studies were unsuccessful. However, a molecular weight determination in acetonitrile by the Signer method[18] gave a value of 665 (calc. 709 for a monomeric species). This, taken together with a conductivity

**Table 1** Selected bond lengths (Å) and angles (°) for [{MnI$_2$-[P(NMe)$_2$]$_3$}$_2$] **1**

| | | | |
|---|---|---|---|
| I(1)–Mn(1) | 2.757(4) | Mn(1)–I(1)–Mn(1′) | 102.5(8) |
| I(1)–Mn(1′) | 2.758(4) | I(1)–Mn(1)–I(1′) | 99.75(8) |
| I(3)–Mn(1) | 2.618(3) | I(1)–Mn(1)–I(3) | 110.7(1) |
| Mn(1)–P(1) | 2.556(6) | I(1)–Mn(1)–P(1) | 108.4(1) |
| P(1)–N(1) | 1.65(1) | Mn(1)–P(1)–N(1) | 111.0(5) |
| P(1)–N(2) | 1.67(1) | N(1)–P(1)–N(2) | 101.7(7) |
| P(1)–N(3) | 1.63(2) | | |

**Table 2** Fractional atomic coordinates for the non-hydrogen atoms of [{MnI$_2$[P(NMe$_2$)$_3$]}$_2$] **1**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| I(1) | 0.389 5(1) | 0.143 0(1) | 0.412 25(7) |
| I(2) | 0.485 3(1) | 0.234 2(1) | 0.693 23(8) |
| Mn(1) | 0.584 9(2) | 0.126 5(2) | 0.571 9(1) |
| P(1) | 0.811 5(4) | 0.242 0(4) | 0.561 0(2) |
| N(1) | 0.936(1) | 0.229(1) | 0.653 2(8) |
| N(2) | 0.796(1) | 0.405(1) | 0.549 5(8) |
| N(3) | 0.868(1) | 0.198(1) | 0.477(1) |
| C(1) | 0.941(2) | 0.120(2) | 0.710(1) |
| C(2) | 1.060(2) | 0.312(3) | 0.673(1) |
| C(3) | 0.764(2) | 0.481(2) | 0.619(2) |
| C(4) | 0.710(2) | 0.453(2) | 0.467(2) |
| C(5) | 0.819(2) | 0.083(2) | 0.424(1) |
| C(6) | 0.983(2) | 0.268(2) | 0.452(1) |

measurement, 2.2 $\Omega^{-1}$ for a $10^{-3}$ mol dm$^{-3}$ solution in nitrobenzene, and the spin-only magnetic moment, points to a monomeric molecular formulation for **2**.

The solid-state low-frequency Raman spectra of **2** and of the parent ligand[19] PI$_2$(C$_6$H$_4$SMe-*o*)$_3$ are compared in Fig. 2. The strong ν(P–I) band at 162 cm$^{-1}$ present in the spectrum of the latter is, as expected, absent in the spectrum of **2**. However, the Raman spectrum of **2** exhibits bands at 187 and 356 cm$^{-1}$, absent in the spectrum of PI$_2$(C$_6$H$_4$SMe-*o*)$_3$ and, by comparison with reported values,[20] the band at 187 cm$^{-1}$ is assignable to terminal ν(Mn–I) [and markedly different to values of *ca.* 120 cm$^{-1}$ reported for bridging ν(Mn–I) bonds[20]], again supporting a monomeric structure. The band at 356 cm$^{-1}$ is at a similar frequency to previous reports[21] for ν(Mn–S), thus indicating that the tertiary phosphine moiety P(C$_6$H$_4$SMe-*o*)$_3$ is acting as a chelating ligand. A further new band at 134 cm$^{-1}$ may be tentatively assigned to ν(Mn–P).

Although we have not been able to obtain a single-crystal structure of **2**, complexes of nickel(II) with P(C$_6$H$_4$SMe-*o*)$_3$ have been investigated[22] and the ability of P(C$_6$H$_4$SMe-*o*)$_3$ to act as a multidentate ligand has been recognised. For example, in [NiCl{P(C$_6$H$_4$SMe-*o*)$_3$}]ClO$_4$ the ligand is tetradentate towards nickel(II).[23] However, considering the evidence presented here that **2** is a monomeric species with two co-ordinated iodines, it would seem certain that P(C$_6$H$_4$SMe-*o*)$_3$ is acting as a P,S bidentate system.

## Conclusion

The complex [{MnI$_2$[P(NMe$_2$)$_3$]}$_2$] represents the only simple manganese phosphine complex which has a dimeric structure and is in complete contrast to previously characterised complexes of this stoichiometry. The reason why the complex adopts this structure may be related to the high basicity and large steric requirements of the phosphine. The complex is also a further example of the unusual types of products available from the simple reaction of dihalogenotriorganophosphorus compounds with metal powders.

The complex [MnI$_2${P(C$_6$H$_4$SMe-*o*)$_3$}] is a simple monomeric tetrahedral complex in which the phosphine ligand acts as a bidentate chelating moiety with the phosphorus and one sulfur atom co-ordinated to the manganese. The isolation of this complex is interesting, since it illustrates that a variety of metal complexes containing a chelating ligand may be available in a simple one-step reaction of substituted dihalogenotriarylphosphorus compounds with metal powders.

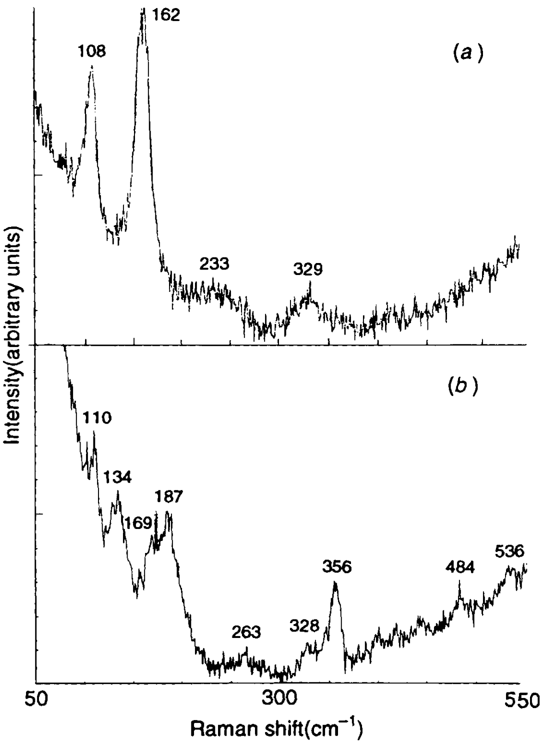

**Fig. 2** A comparison of the low-frequency Raman spectra of PI$_2$(C$_6$H$_4$-SMe-*o*)$_3$ (*a*) and complex [MnI$_2${P(C$_6$H$_4$SMe-*o*)$_3$}] **2** (*b*)

## Experimental

All manganese–phosphine complexes are moisture sensitive, as are the diiodotriorganophosphorus compounds, R$_3$PI$_2$. Therefore strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box (dioxygen concentration < 100 ppm). The synthesis and characterisation of PI$_2$(C$_6$H$_4$SMe-*o*)$_3$ has been described elsewhere.[19] The phosphine PI$_2$(NMe$_2$)$_3$ was synthesised in an identical manner from the direct reaction of (redistilled) commercially obtained P(NMe$_2$)$_3$ (Janssen) with I$_2$ in diethyl ether [Found: C, 17.0: H, 4.3; I, 61.4; N, 9.8. PI$_2$(NMe$_2$)$_3$ requires C, 17.3; H, 4.3; I, 60.9; N, 10.1%]. Standard reagent-grade coarse-grain manganese powder was obtained commercially (Aldrich) and used as received.

Diethyl ether (BDH) was dried over sodium wire for *ca.* 1 d and subsequently distilled over CaH$_2$ in an inert (N$_2$) atmosphere. Both the complexes described here were synthesised by the published method[6] *viz.* the direct reaction of manganese metal powder with the diiodotriorganophosphorus compound in diethyl ether (Found: C, 15.3; H, 3.8; I, 35.4; N, 8.9. [{MnI$_2$[P(NMe$_2$)$_3$]}$_2$] **1** requires C, 15.3; H, 3.8; I, 35.8; N, 8.9. Found: C, 35.4; H, 2.9; I, 36.4; Mn, 6.7; P, 4.2. [MnI$_2${P(C$_6$H$_4$SMe-*o*)$_3$}] **2** requires C, 35.5; H, 3.0; I, 35.8; Mn, 7.7; P, 4.4%). Reaction times are approximately 5 d. Elemental analyses were performed by the analytical laboratory of this department. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 SW argon-ion laser and a SPEX 1403 0.85 m focal length double monochromator fitted with BGCS microscope sampling attachment. The radiation was detected using a Hamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products

**Table 3** Crystal data and details of refinement for $[\{MnI_2[P(NMe_2)_3]\}_2]$ **1**

| | |
|---|---|
| Formula | $C_{12}H_{36}IMn_2N_6P_2$ |
| *M* | 943.90 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$/Å | 9.777(7) |
| $b$/Å | 10.166(5) |
| $c$/Å | 15.915(4) |
| $\beta$/° | 105.06(3) |
| $U$/Å$^3$ | 1527(2) |
| $Z$ | 2 |
| $D_c$/g cm$^{-3}$ | 2.052 |
| $F$(000) | 884 |
| $\mu$/cm$^{-1}$ | 49.10 |
| Crystal size/mm | 0.3 × 0.3 × 0.1 |
| Decomposition (%) | 11 |
| $\omega$ Scan width/° | $1.13 + 0.3\tan\theta$ |
| Maximum $\theta$/° | 25 |
| Maximum, minimum transmission[a] | 0.68, 1.00 |
| Total data measured | 3032 |
| Number of unique reflections | 2854 |
| Number of observed reflections $[F_o < 3\sigma(F_o)]$ | 1111 |
| Number of parameters | 118 |
| $\rho_{min}, \rho_{max}$/e Å$^{-3}$ | −0.83, 0.98 |
| Maximum least-squares shift-to-error ratio | 0.01 |
| Weighting scheme parameter $g$ in $w = 1/[\sigma^2(F) + gF^2]$ | 0.03 |
| Final $R$ | 0.041 |
| Final $R'$[b] | 0.043 |

[a] Absorption correction by azimuthal scan technique. [b] Function minimized $\Sigma w(|F_o| - |F_c|)^2$.

for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station.

The magnetic moments were recorded on a Johnson Matthey Faraday balance. The molecular weight measurement of $[MnI_2\{P(C_6H_4SMe\text{-}o)_3\}]$ in acetonitrile was made using the Signer method.[18] The electrical conductivity of an acetonitrile solution of $[\{MnI_2[P(NMe_2)_3]\}_2]$ was recorded using an Oxford Instruments conductivity bridge.

*Crystallography.*—Crystal data and details of refinement for $[\{MnI_2[P(NMe_2)_3]\}_2]$ are presented in Table 3. A pink crystal was mounted in a Lindemann tube under an atmosphere of dry argon. All measurements were performed on a Rigaku AFC6S diffractometer employing graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å) and $\omega$–2$\theta$ scans.

The structure was solved by direct methods using SHELX 86[24] and refined by full-matrix least squares based on $F$ using TEXSAN.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to chemically reasonable positions (C–H = 0.95 Å) with isotropic thermal parameters set at 120% of the equivalent $B$ values of the bonded atom. Neutral atom scattering factors were used throughout.[26] Fractional atomic coordinates and some details of molecular geometry are listed in Tables 1 and 2 respectively.

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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