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REACTIVITY OF TETRASULFUR TETRANITRIDE TOWARDS d^{10} PHOSPHINE COMPLEXES. CRYSTAL STRUCTURE OF $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$

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Summary

Tetrasulfur tetranitride reacts with $(PPh_3)_2M(C_2H_4)$, M = Pd, Pt, or $[(PPh_3)_2Ni(C_3Ph_3)]ClO_4$ to give the compounds $(PPh_3)M(\mu\text{-}S_2N_2)_2M(PPh_3)$. A complete X-ray structure determination has been carried out on the platinum derivative. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with a 14.872(10), b 14.920(10), c 9.255(6) Å, β 98.93(4)°, $Z = 4$. The structure was solved by the heavy atom method and refined by full-matrix least-squares to the conventional R factor of 0.063 for 811 observed reflections. The structure consists of centrosymmetric dinuclear complexes in which the metal atoms are bridged by two S_2N_2 fragments. Each S_2N_2 group acts as a bidentate ligand bridging the metal centers through a nitrogen and coordinating to only one metal through a sulfur atom. A triphenylphosphine ligand completes a square planar environment around each metal atom.

Introduction

Tetrasulfur tetranitride is known to react with Lewis acids such as $AlCl_3$, $SnCl_4$, VCl_4, WCl_4, $NiCl_2$, $CuCl_2$ etc. in two main ways (a) with preservation of the S_4N_4 ring [1], and (b) with ring cleavage, to form the S_2N_2 ring [2] or metal-sulfur-nitrogen heterocycles [3]. There have, however, been few reports of reactions of S_4N_4 with transition metal complexes in low-oxidation states [4], but the facile nucleophilic degradation of this molecule (e.g. by phosphines [5]) suggests that a wide range of complexes could be obtained by reaction with nucleophilic or radical-type complexes. The range of reactions of the related S_8 species is in agreement with this hypothesis [6].

We now report the syntheses of the complexes $[(PPh_3)M(S_2N_2)]_2$ where M = Ni, Pd, Pt, which were obtained by treating S_4N_4 with $(PPh_3)_2M(C_2H_4)$ (M = Pd, Pt) or

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$[(PPh_3)_2Ni(C_3Ph_3)]\ ClO_4$. A complete X-ray structure determination has been carried out on the platinum complex.

A previous paper described the syntheses of the two complexes $(PPh_3)_2Pt(S_4N_4)$ and $(PPh_3)_2Pt(S_2N_2)$, obtained by the reaction of S_4N_4 with $(PPh_3)_4Pt$ [4a]. These compounds, for which the X-ray structures have so far not been reported, were formulated only on the basis of approximate elemental analyses.

Results and discussion

Synthesis and chemical characterization. Tetrasulfur tetranitride reacts rapidly at room temperature under nitrogen with $(PPh_3)_2Pt(C_2H_4)$ in tetrahydrofuran to form a green solution. This solution slowly turns brown and then red brown crystals separate, which analyse as $(PPh_3)Pt(S_2N_2)$. The compound is air-stable, and practically insoluble in common organic solvents such as methylene chloride, acetone, tetrahydrofuran, and benzene. As indicated by the X-ray study below, the structure consists of dimeric complex molecules $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$ (**1**).

When the reaction of S_4N_4 with $(PPh_3)_2Pt(C_2H_4)$ at room temperature under nitrogen is carried out in benzene instead of tetrahydrofuran, a largely similar reaction occurs and the dimeric solvate complex $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)\cdot C_6H_6$ (**2**) is formed *. Compound **2** is isomorphous with complex **1** **. However, if more concentrated solutions are kept at 8°C, the dark-green benzene solution deposits thin yellow crystals (**3**); these crystals are air-stable, and very soluble in methylene chloride, acetone and tetrahydrofuran to yield a yellow solution, which turns brown in 3–4 min. From these solutions red-brown crystals of the dimeric complex $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$ rapidly separate. The intermediate complex **3** analyses as $Pt_2(PPh_3)_3(S_4N_4)\cdot C_6H_6$. The mass spectrum of (**3**) (EI, T 150°C), which clearly shows the presence of solvate benzene, does not contain any signal attributable to S_4N_4 or fragments derived from it and so the possibility that compound **3** is an adduct of the $Pt(PPh_3)_2$ moiety with N_4S_4 or N_2S_2 rings can be ruled out [2c]. Thus it is likely that in this compound the sulfur and nitrogen atoms are again involved in a metal heterocycle such as $\overline{\text{PtNSNS}}$; the mass spectrum of compound **1** recorded under identical conditions also shows no signals attributable to $\overline{\text{MNSNS}}$ heterocycles or S_xN_y groups.

On the basis of the available data the formulation $(PPh_3)_2Pt(\mu\text{-}S_2N_2)\text{-}Pt(S_2N_2)(PPh_3)\cdot C_6H_6$ can be tentatively assigned to complex **3**. However, the poor quality of the crystals has so far prevented a complete structural elucidation by X-ray diffraction.

Upon treating $(PPh_3)_2Pd(C_2H_4)$ with S_4N_4 the dimeric complex $(PPh_3)Pd(\mu\text{-}S_2N_2)_2Pd(PPh_3)$ (**4**) is rapidly and exclusively formed; thus must have a structure exactly like that of the platinum complex.

In the reactions of S_4N_4 with $(PPh_3)_2Ni(C_2H_4)$ under various reaction conditions (variation of solvent and temperature) a dusty red analytically ill-defined material is always formed. However, treatment of S_4N_4 with $[(PPh_3)_2Ni(C_3Ph_3)]ClO_4$ *** in

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* The presence of solvate benzene is clearly shown by the mass spectrum.

** Monoclinic, space group $P2_1/n$, a 14.534(12), b 15.246(13) c 9.392(8) Å, β 99.80(6)°.

*** This derivative, probably owing to the smaller lability of C_3Ph_3 with respect to C_2H_4, allowed the isolation of crystals of $(PPh_3)Ni(CS_2)_2Ni(PPh_3)$ [7].

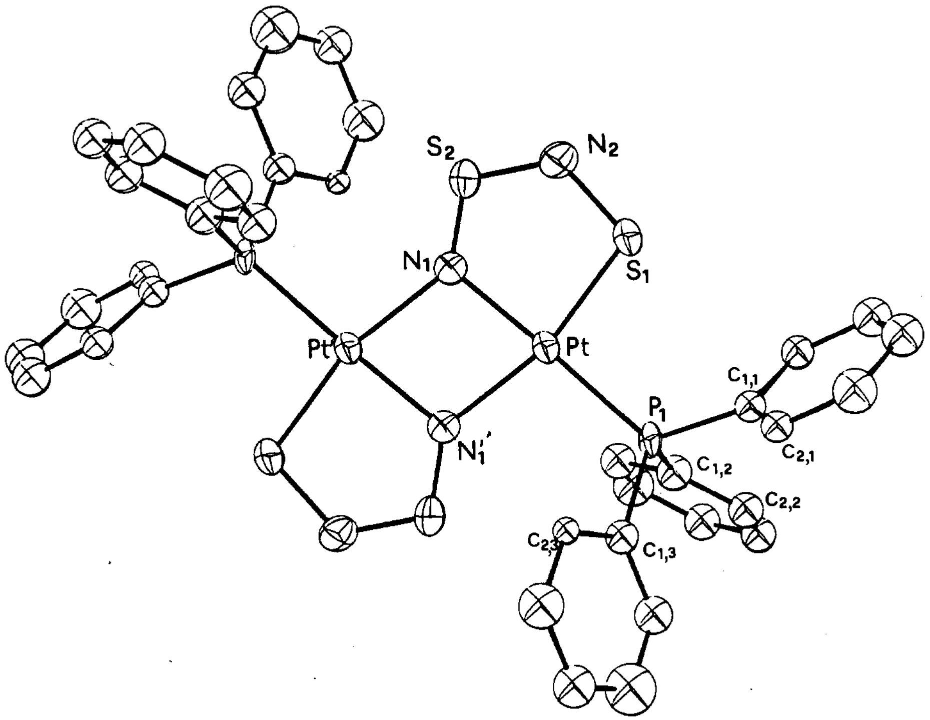

Fig. 1. Perspective view of the complex molecule $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$. ORTEP drawing with 30% probability ellipsoids.

methylene chloride gave a few thin brown-red crystals. Preliminary X-ray data have shown that this compound (**5**) is isostructural with the platinum complex **1** *.

Description of the structure. In the dimeric complex molecule which possesses C_i-$\bar{1}$ crystallographic symmetry, the two metal centres are held together by two S_2N_2 units. Each S_2N_2 group, acting as bidentate ligand, bridges two platinum atoms through a nitrogen atom and coordinates to one metal through a sulfur atom. A triphenylphosphine ligand completes the coordination around the metal atom, which displays a distorted square planar geometry. All the atoms of the coordination polyhedra are almost coplanar, the largest deviation from the least-square plane being 0.04 Å. Figure 1 shows a perspective view of the molecule and Table 1 lists selected bond distances and angles.

Among the bond distances involving the platinum atom, a shortening is observed with respect to the sum of covalent radii for Pt–N(1) (1.98(4) vs. 2.05 Å), Pt–S(1) (2.225(13) vs. 2.32 Å) and Pt–P(1) (2.265(13) vs. 2.36 Å). The fourth ligand N(1') is at a significantly larger distance (2.12(4) vs. 2.05 Å). A similar feature is observed in the tetraphenylarsonium salt $[Ph_4As]_2[Ni_2(S_2N_2)_2(CN)_2]$ **, which contains the

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* Monoclinic, space group $P2_1/n$, a 14.295(10), b 14.615(11), c 9.375(7) Å, β 98.27(5)°.

** This complex was prepared following a procedure different from that used for the title compounds viz. by dehydrogenating the complex $Ni(HN_2S_2)_2$.

same bridging S_2N_2 group and shows a similar stereochemistry [8]. On the other hand the Pt–P bond distance is comparable with the values reported for $(PPh_3)_2Pt(S_4)$ [9] and $(PPh_3)_2Pt(SH)_2$[10]. The Pt–S bond is shorter than those in the latter compounds, but is in good agreement with the values found in the $Pt(S_2CC_6H_4\text{-i-Pr})(S_3CC_6H_5\text{-i-Pr})$ complex [11], in which the PtS_3C fragment is planar.

The S_2N_2 unit can be viewed as being generated from the cleavage of the cyclic S_2N_2 group and adding oxidatively to the metal(0) centre. Interestingly the electronic redistribution which takes place in the group upon its liberation and subsequent coordination leads to a more localized structure. Indeed, while in the S_2N_2 free group [12] and in the bidentate-S_2N_2 adducts [2] the S–N bond distances are equivalent and indicative of some delocalized multiple bond character, in our compound the three S–N distances are unequal, ranging from 1.51(3) to 1.66(4) Å. An even larger difference is observed in the $[Ni_2(S_2N_2)_2(CN)_2]^{2+}$ derivative [8], where one S–N bond distance of 1.78 Å clearly suggests a single bond while the other two S–N distances (1.58 and 1.54 Å) indicate multiple bond character. (The S–N single bond should be approximately 1.74 Å, and the S–N double bond ca. 1.54 Å) [12]. An electronic distribution of this type is also observed in some monomeric metal S_2N_2 complexes, such as $[Ni(HN_2S_2)(N_2S_2)]^-$ [13], $[Ni(HN_2S_2)(S_2N_2R)]^-$ [14] and $CpCo(S_2N_2)$ [4c]. Some degree of bond fixation has been noted also in a Ru–S_2N_2 complex, where the cyclic S_2N_2 group acts as monodentate bridging ligand, and an explanation has been suggested on the basis of the interactions involving the sulfur atoms of the ring [2c]. In our compound, however, the shortest non-bonded contacts involving the sulfur atoms fall within the normal limits.

The bond angles around the platinum atom are consistent with a distorted square planar geometry; the distortion from the idealized values seems mainly due to the constraints imposed by the presence of a four- and a five-membered ring. Moreover the presence of the bulky triphenylphosphine increases the widening of the angles involving the phosphorus atom (101.2(11), 95.1(5)°), with consequent narrowing of the others (76.4(15), 87.3(11)°). In the nickel-analogue $[Ni_2(S_2N_2)_2(CN)_2]^{2+}$ the

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) IN $(PPh_3)(Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$

Pt–P(1)	2.265(13)	S(2)–N(2)	1.58(4)
Pt–S(1)	2.225(13)	N(1)–S(2)	1.51(3)
Pt–N(1)	1.98(4)	P(1)–C(1,1)	1.82(3)
Pt–N(1′)	2.12(4)	P(1)–C(1,2)	1.84(4)
S(1)–N(2)	1.66(4)	P(1)–C(1,3)	1.80(3)
P(1)–Pt–S(1)	95.1(5)	C(1,1)–P(1)–C(1,2)	104.0(13)
P(1)–Pt–N(1)	177.1(11)	C(1,1)–P(1)–C(1,3)	104.4(13)
P(1)–Pt–N(1′)	101.2(11)	C(1,2)–P(1)–C(1,3)	107.5(13)
S(1)–Pt–N(1)	87.3(11)	Pt–S(1)–N(2)	103.7(14)
S(1)–Pt–N(1′)	163.6(11)	N(1)–S(2)–N(2)	111.9(21)
N(1)–Pt–N(1′)	76.4(15)	Pt–N(1)–S(2)	119.4(23)
Pt–P(1)–C(1,1)	117.2(10)	Pt–N(1)–Pt′	103.6(17)
Pt–P(1)–C(1,2)	112.4(10)	S(2)–N(1)–Pt′	137.1(24)
Pt–P(1)–C(1,3)	110.6(10)	S(1)–N(2)–S(2)	117.6(24)

triphenylphosphine is replaced by a CN group, and the distortion is consistent with a smaller hindrance by the group [8].

The angles within the S_2N_2 unit are comparable with those in polymeric $(SN)_x$ [15], in which the N–S–N and S–N–S angles of 106.2(2) and 119.9(4)° are consistent with the sp^3 and sp^2 hybridization states of the sulfur and nitrogen atoms, respectively.

Conclusions

The reactions of S_4N_4 with d^{10} metals lead to d^8 square planar metal complexes, containing the chelating ligand $[S{-}N{-}S{-}N]^{2-}$. Thus the heterocycles $\overline{\text{MNSNS}}$ must be regarded as arising from oxidative-addition of an S_2N_2 fragment to the metal atom. The S_4N_4 is, as expected, nucleophilically degraded by the electron-rich metal centers. This view is confirmed by the reaction of S_4N_4 with the d^8 iridium complex $[(Ph_2PCH{=}CHPPh_2)_2Ir(CO)]BPh_4$, which leads to the octahedral derivative of iridium(III) $[(Ph_2PCH{=}CHPPh_2)_2Ir(S_2N_2)]BPh_4$ [16].

Experimental

The reactions were carried out under oxygen-free nitrogen. All solvents were reagent grade and were used without further purification. The complexes $(PPh_3)_2Pt(C_2H_4)$ [17], $(PPh_3)_2Pd(C_2H_4)$ [18] and $[(PPh_3)_2Ni(C_3Ph_3)]ClO_4$ [19] were prepared by published methods. Tetrasulfur tetranitride was prepared by the standard method [20] and crystallised several times from CH_2Cl_2 before use. Mass spectra were recorded at 70 eV on a Kratos MS80 spectrometer. A direct insertion probe was employed with source temperature of 100–150°C.

Reaction of S_4N_4 with $(PPh_3)_2Pt(C_2H_4)$. (a) A solution of S_4N_4 (75 mg, 0.4 mmol) in benzene (30 cm^3) was added to a solution of $(PPh_3)_2Pt(C_2H_4)$ (300 mg, 0.4 mmol) in tetrahydrofuran (15 cm^3). Red-brown crystals of $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)$ (**1**) quickly separated, and were collected, washed with methylene chloride, benzene, and light petroleum, then dried. Yield: 100 mg (50%). (Found: C, 40.72; H, 3.24; N, 4.44; S, 11.35. $C_{36}H_{30}N_4P_2Pt_2S_4$ calcd.: C, 39.34; H, 2.75; N, 5.09; S, 11.67%).

(b) A solution of tetrasulfur tetranitride (75 mg, 0.4 mmol) in benzene (20 cm^3) was added to a solution of $(PPh_3)_2Pt(C_2H_4)$ (300 mg, 0.4 mmol) in benzene (10 cm^3) at room temperature. The resulting green solution slowly turned brown, and red-brown crystals of the complex $(PPh_3)Pt(\mu\text{-}S_2N_2)_2Pt(PPh_3)\cdot C_6H_6$ (**2**) separated. The crystals were filtered off, washed with methylene chloride, and light petroleum, then dried. Yield: 150 mg (70%). (Found: C, 43.67; H, 3.08; N, 4.87. $C_{36}H_{30}N_4P_2Pt_2S_4\cdot C_6H_6$ calcd.: C, 42.85; H, 3.08; N, 4.76%). The mass spectrum (EI, T 150°C) clearly shows the presence of solvate benzene ($m/e = 78$, 100%) *. An X-ray study showed that this compound is isomorphous with **1**.

(c) A solution of tetrasulfur tetranitride (75 mg, 0.4 mmol) in benzene (10 cm^3) was added to a solution of $(PPh_3)_2Pt(C_2H_4)$ (300 mg, 0.4 mmol) in benzene (5 cm^3)

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* The isotope pattern rules out the presence of the NS_2 group.

TABLE 2

CRYSTAL DATA AND DETAILS OF DATA COLLECTION

mol formula	$C_{18}H_{15}N_2PPtS_2$	dimension (mm)	0.300 × 0.033 × 0.017
mol wt	549.52	color	red-brown
a (Å)	14.872(10)	diffractometer	Philips PW 1100
b (Å)	14.920(10)	monochromator	graphite crystal
c (Å)	9.255(6)	method	ω-2θ scan technique
β, deg	98.93(4)	scan speed (deg/s)	0.05
d_{calcd} (g cm^{-3})	1.799	scan width (deg)	$0.70 + 0.3 \tan\theta$
V, Å^3	2028.7	background	half the scan time
space group	$P2_1/n$	standards	3 every 120 readings
Z	4	max. dev. of standards (%)	4
abs coeff (μ(Mo-K_α)), cm^{-1}	72.6	octants collected	$\pm h$, $+k$, $+l$
transm. factors, range	0.885–0.783	2θ limits, deg	5–50
habitus	regular parallelepiped	number of data with $I \geqslant 3\sigma(I)$	811
		final number of variables	93

at 8°C. The resulting green solution gave yellow crystals of $(PPh_3)_2Pt(\mu\text{-}S_2N_2)Pt(S_2N_2)(PPh_3) \cdot C_6H_6$ (3) within 10 min. Yield: 115 mg (40%). (Found: C, 49.16; H, 3.40; N, 3.86; P, 6.10; Pt, 25.78; S, 8.77. $C_{54}H_{45}P_3Pt_2N_4S_4 \cdot C_6H_6$ calcd.: C, 50.06; H, 3.57; N, 3.89, P, 6.45; Pt, 27.10; S, 8.90%). The mass spectrum (EI, T 150°C) clearly shows the presence of solvate benzene ($m/e = 78$, 100%) *.

Preparation of $(PPh_3)Pd(\mu\text{-}S_2N_2)Pd(PPh_3)$ complex (4). This complex was prepared by the procedure used for the platinum derivative **1** from reacting S_4N_4 and $(PPh_3)_2Pd(C_2H_4)$ in 1/1 ratio. Yield: 50%. (Found: C, 46.95; H, 4.20; N, 5.66; S, 13.35. $C_{36}H_{30}N_4P_2Pd_2S_2$ calcd.: C, 46.91; H, 3.28; N, 6.08; S, 13.52%).

Reaction of S_4N_4 with $[(PPh_3)_2Ni(C_3Ph_3)]ClO_4$ (5). Solid S_4N_4 (75 mg, 0.4 mmol) was added to a solution of $[(PPh_3)_2Ni(C_3Ph_3)]ClO_4$ (380 mg, 0.4 mmol) in methylene chloride (40 cm^3). The solution immediately turned red-brown and a few thin insoluble crystals were formed. (Yield: 10 mg (5%)). Preliminary X-ray data indicated the formation of the dinuclear complex $(PPh_3)Ni(\mu\text{-}S_2N_2)_2Ni(PPh_3)$.

Collection and reduction of X-ray intensity data. A small well formed crystal was mounted on a Philips PW 1100 automatic diffractometer. The setting angles of 20 carefully centered reflections were used to determine by least-squares refinement the unit cell parameters. Systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ were consistent with the space group $P2_1/n$. Crystal data and details of the data collection are given in Table 2. The procedure followed in the data processing has been described elsewhere [21]. After correction for background, the intensities I were assigned standard deviations $\sigma(I)$ calculated, as previously, by using a value of 0.03 for the instability factor p [22]. The intensity data were corrected for Lorentz and polarization effects and for absorption effects. Anomalous dispersion effects were taken into account in the F_c calculations [23].

Determination and refinement of the structure. All calculations were carried out using the SHELX 76 crystallographic system of programs on a SEL 32/77 computer, in this Institute [24]. Neutral atom scattering factors for non-hydrogen atoms were taken from ref. 25, and those for hydrogen atoms from ref. 26. The refinements

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* The isotope pattern rules out the presence of the NS_2 group.

TABLE 3

POSITIONAL PARAMETERS ($\times 10^4$)

Atom	*x*	*y*	*z*
Pt	727(1)	793(1)	−57(3)
P(1)	2094(9)	984(8)	−807(13)
S(1)	623(9)	2198(8)	708(16)
S(2)	−891(9)	1303(11)	1375(18)
N(1)	−449(25)	564(26)	626(37)
N(2)	−333(23)	2202(26)	1431(41)
C(1,1)	2772(19)	1948(16)	−83(30)
C(2,1)	3436(19)	1858(16)	1150(30)
C(3,1)	3851(19)	2619(16)	1833(30)
C(4,1)	3601(19)	3469(16)	1282(30)
C(5,1)	2937(19)	3558(16)	49(30)
C(6,1)	2522(19)	2797(16)	−633(30)
C(1,2)	1990(17)	1114(18)	−2804(36)
C(2,2)	2709(17)	1470(18)	−3424(36)
C(3,2)	2646(17)	1525(18)	−4941(36)
C(4,2)	1863(17)	1224(18)	−5838(36)
C(5,2)	1144(17)	868(18)	−5219(36)
C(6,2)	1207(17)	812(18)	−3702(36)
C(1,3)	2823(19)	33(19)	−293(30)
C(2,3)	2720(19)	−470(19)	942(30)
C(3,3)	3258(19)	−1227(19)	1303(30)
C(4,3)	3899(19)	−1482(19)	429(30)
C(5,3)	4002(19)	−979(19)	−805(30)
C(6,3)	3464(19)	−221(19)	−1166(30)

were based on F_0, the function minimizing being $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2(F_0)$. The structure was solved by the heavy atom method; a Patterson map revealed the platinum atom position, and from successive Fourier syntheses all non-hydrogen atoms were located. The structure was refined by full-matrix least-squares techniques using anisotropic thermal parameters for Pt, P, S and N atoms. The phenyl rings of the phosphine ligand were treated as rigid bodies of D_{6h} symmetry, pivoting on the carbon atom attached to phosphorus. Hydrogen atoms, which were introduced in their calculated positions, were not refined. The final R and R_w factors are 0.063 and 0.057 respectively. Table 3 lists final positional parameters. Tables of structure factors, H-atom coordinates and thermal parameters are available from the authors.

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