Thiolate Complexes of Gold(I) Based on a Tris(phosphine) Support

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Treatment of the ligand 1,3,5-tris[(diphenylphosphanyl)methyl]trimethylbenzene (P₃) with (tetrahydrothiophene)gold(I) chloride results in the symmetrical trigold complex [(P₃)(AuCl)₃]. In the presence of sodium methoxide, [(P₃)(AuCl)₃] reacts with thiocresol (HSC₆H₄Me-4) and 2-mercaptoquinoline (2-HSQn) to provide the complexes [(P₃)(AuSC₆H₄Me-4)₃] and [(P₃)(AuSQn)₃], respectively. Reaction of [(P₃)(AuCl)₃] with KSCN also yields the expected product [(P₃)(AuSCN)₃], however, treatment with 2 - 10 molar equivalents of NaSMe results only in the unsymmetrical cationic complex [(P₃)Au₃(SMe)₂]Cl. Reaction between [(P₃)(AuOTf)₃] (prepared *in situ* from [(P₃)(AuCl)₃] and AgOTf) and sodium sulfide yields the complex [(P₃)Au₃S]⁺OSO₂CF₃⁻, the first example of a trigoldsulfonium unit coordinated to a tridentate phosphine. The tetrafluoroborate salt is obtained from [(P₃)(AuCl)₃] and Na₂S · 9 H₂0 in the presence of NaBF₄. The structure of [(P₃)(AuSMe)₂]Cl has been determined and reveals that in the solid the two methylthiolate units bridge the three gold atoms, but the structure of the cation is fluxional in solution according to NMR data.

Introduction

Gold metal has a remarkable affinity for the heavier chalcogen elements and a large number of compounds with sulfur donors have been reported [1]. Thiolate complexes make up the most common class of gold(I) compounds with sulfur and many applications (medicine [2], self-assembly monolayers [3], liquid golds for ceramics [4]) have been found for this class of compounds. Some early observations in sulfur chemistry were followed by the preparation of the synthetically highly versatile oxonium salts $[O(AuPPh_3)_3]^+$ in 1980 [5], which are analogues of the corresponding complexes of the heavier chalcogen elements $[A(AuPPh_3)_3]^+$ (A = S, Se, Te [6, 7]). These thrice aurated complexes are among the bestknown examples of multiply-aurated main group elements (C, N, P, S, Se, Te). In many cases, the synthesis can be broken down into individual auration steps involving the successive addition of [AuPR₃]⁺ units. These results have shown that auration of sulfide goes well beyond the 2:1 stoichiometry of Au₂S [8].

The coordination of gold(I) centers to tridentate tertiary phosphine ligands has been the subject of a number of reports. The tris[2-(diphenylphosphino)ethyl)lamine ligand (NP₃) was found to react with [LAuCl] (L = tetrahydrothiophene, PPh_3) to give the cations $[Au(NP_3)]^+X^-$ (X = Cl⁻, PF₆⁻, NO_3^- , Scheme 1, a) for which X-ray structures (of the PF_6^- and NO_3^- salts) were established [9]. It was discovered that if BPh₄⁻ was employed as a counteranion, a quite different structure was adopted in which each of two NP₃ ligands binds in a bidentate manner at one gold atom while the third phosphine 'arm' reaches across to bind to the second gold center (Scheme 1, b). The complexes $ClAuP[(CH_2)_nPPh_2AuCl]_2$ (*n* = 1 [10], *n* = 2 [11]) shown in Scheme 1, c have also been prepared and used in the synthesis of thiolate complexes [12]. Both complexes display gold-gold contacts between the three gold atoms. The trication 'sandwich' complex [$\{Ph_2PCH_2P(Ph)CH_2PPh_2\}_2Au_3$](SCN)₃ [13] (Scheme 1, d) has been prepared directly from KAuCl₄ and the ligand in the presence of NaSCN and bis(2-hydroxyethyl)sulfide. The structure of the complex displays particularly short aurophilic interactions in the range 2.95 - 2.96 Å.

A recent report from these laboratories concerned the preparation of the complex $[Ph(ClAu)P\{C_6H_4P(AuCl)Ph_2-2\}_2]$ (Scheme 1, e) from the tridentate phosphine $[PhP(C_6H_4PPh_2-2)_2]$.

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Scheme 1. A selection of reported [tris(phosphine)]gold(I) compounds, and complex $h = [(P_3)(AuCl)_3]$ (1).

A variable temperature NMR study performed on this system proved that the aurophilic contacts found in the solid state persist in solution [14] and that the bond energy was also in good agreement with that calculated previously [15].

The structure of the tri[chlorogold(I)] complex of the tris(diphenylphosphino)methane (tppm) ligand [(tppm)(AuCl)₃] (Scheme 1, **f**) was found to contain aurophilic contacts of 3.20 Å [16], however, the related bis(tppm) complex [Au₂(tppm)(AuCl)](ClO₄)₂ (Scheme 1, **g**) displays even shorter distances between gold atoms (2.92 -3.09 Å) due to a constrained geometry [17].

Recent research in these laboratories has centered on tailoring ligands to provide a favorable coordination geometry for the attached gold centers [14, 16, 18]. Such a ligand was provided by the synthesis of the species 1,4-bis(diphenylphosphanylmethyl)benzene which provided the requisite 90° angle for the coordination of an [AuS₂] unit [18]. This led us to prepare a tris(phosphine) variant with an even greater degree of flexibility in the phosphine 'arms'. We present here the results of an investigation into the coordination chemistry of this ligand, 1,3,5-tris[(diphenylphosphanyl)methyl]trimethylbenzene (P₃), with gold(I) (Scheme 1, **h**), and the subsequent reactivity with sulfur donors.

Synthesis and Characterization of Complexes

The tris(phosphine) ligand 1,3,5-tris[(diphenylphosphanylmethyl)trimethylbenzene] (P₃) was found to react cleanly with three molar equivalents of either (tht)AuCl or (Me₂S)AuCl to provide the

desired trigold complex $[(P_3)(AuCl)_3]$ (1) in excellent yield (Scheme 2). A singlet was observed in the ³¹P NMR spectrum at 29.9 ppm indicating a symmetrical geometry for the complex in solution. Singlet (1.78 ppm) and doublet (3.84 ppm, $J_{PH} =$ 13.0 Hz) resonances were observed in the ¹H NMR spectrum for the methyl and methylene protons, respectively. The singlets at 135.8 ($C^{2,4,6}C_6Me_3$) and 131.0 ($C^{1,3,5}C_6Me_3$) ppm in the ¹³C NMR spectrum are in accordance with the presence of only two carbon environments for the central aromatic ring. In the same spectrum, peaks were observed for the methylene carbon atoms at 31.8 (d, $J_{PC} = 23.0 \text{ Hz}$) ppm whereas the singlet observed at 20.3 ppm was assigned to the methyl carbons. Additional characteristic resonances were present for the aromatic carbon atoms of the other phosphine substituents. Microanalytical data showed that the complex crystallizes as a dichloromethane trisolvate.

The first sulfur donor to be investigated as a ligand for the complex was thiocyanate which reacted to yield the expected compound $[(P_3)(AuSCN)_3]$ (2). A 3:2 ratio was observed in the ¹H NMR spectrum for the methyl and methylene protons and analytical data confirmed the overall molecular composition. The ³¹P NMR spectrum displayed a broad singlet suggesting that the three phosphine 'arms' are not rigidly fixed at room temperature. The same observation was made for all subsequent trithiolate species.

The coordinating abilities of two other thiolates (*p*-thiocresol, 2-mercaptoquinoline) were also examined. These reactions were performed in the presence of sodium methoxide in order to aid deproto-

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Scheme 3. Schematic drawing of the cation in compound 5.

nation of the thiol and led to the complexes $[(P_3)-(AuSC_6H_4Me-2)_3]$ (3) and $[(P_3)(AuSQn)_3]$ (SQn = quinoline thiolate) (4), respectively. The spectroscopic data associated with the tris(phosphine) ligand are found to be almost identical to that obtained for the previous complexes. In the ¹H NMR spectrum, compound 3 showed a number of new resonances attributed to the aromatic protons (6.89, 7.08 ppm, AB system, $J_{HH} = 8.1$ Hz) and methyl protons (2.43 ppm) of the tolylthiolate group. In contrast, however, the peaks due to the quinolinethiolate ligand for complex 4 were not as clearly resolved and were observed as a series of multiplets.

Treatment of complex 1 with three molar equivalents of NaSMe yielded a pale yellow product. The ³¹P NMR spectrum displayed a single broadened peak at 36.4 ppm. However, the integration of the ¹H NMR spectrum for this species

did not provide the expected 2:3 ratio of methylene to S-methyl protons expected for a product of composition [(P₃)(AuSMe)₃], but instead revealed a 1:1 ratio. This indicated formation of a product containing only two methylthiolate ligands. There is precedence for the coordination of more than one gold center to a single sulfur donor (see introduction) and a structural investigation revealed that this had indeed occurred. The identity of the product (Scheme 3) was confirmed as the compound $[(P_3)Au_3(SMe)_2]Cl(5)$ in which the three gold centers are bridged by only two SMe groups (see structural section). If viewed carefully, it becomes apparent that there are similarities between this arrangement and that found in the complexes $[(MeC_6H_4S_2-3,4)(AuPPh_3)_3]^+$ and $[(CH_2S)_2(AuPPh_3)_3]^+$ in which the AuPPh_3 units each bridge two sulfur atoms [19, 20]. What was more unexpected was the fact that the same product was obtained on reaction of $[(P_3)(AuCl)_3]$ (1) with two, three or even ten molar equivalents of sodium methylthiolate. The related bis(phosphine) variants [C₆H₄(CH₂PPh₂AuSMe)₂-1,4] and [C₆H₄-(1,4-CH₂PPh₂Au)₂SMe]BF₄ have been prepared from $[C_6H_4(CH_2Ph_2PAuCl)_2-1,4]$, however, the formation of the different products was determined through varying the stoichiometry of the reagents [12]. This suggests perhaps that the greater flexibility of the P₃ ligand compared to the related 1,4-substituted bis(phosphine) species plays a role in the structure of 5. A comparison of 5 with the other two thiolate complexes $[(P_3)(AuSR)_3]$ [R = C_6H_4Me-4 (3), quinoline (4)] would suggest that a cationic, bridged, dithiolate species is favored for the compact methylthiolate ligand over the conventional trithiolate structure proposed for the complexes 3 and 4. The reasons for this are not entirely clear but the comparatively electron-rich nature of the methylthiolate ligand could provide a clue as to why only two ligands are required for the stability of 5 whereas three thiolate ligands (bearing electron withdrawing tolyl or quinoline substituents) are required for complexes 3 and 4. It is less likely but still possible that steric factors also have a role to play.

Having succeeded in bringing two gold centers together through a sulfur donor, it was clear that the next challenge would be the preparation of a $[(R_3PAu)_3S]^+$ analogue. Two synthetic routes were employed. The first involved the treatment of complex 1 with three equivalents of $AgOSO_2CF_3$ to provide an *in situ* solution of $[(P_3)(AuOTf)_3]$ and subsequent addition of an excess of sodium sulfide. The second was the more direct addition of an aqueous solution of $Na_2S \cdot 9 H_2O$ and $NaBF_4$ to 1. Both were found to yield the desired salts with the cation $[(P_3)Au_3S]^+$ (6) in which all three gold centers are bound to the same sulfur atom. In contrast to the other thiolate complexes discussed above, the ³¹P NMR spectra for **6** displayed a sharp peak at 37.8 ppm indicating a restriction on movement of the phosphine 'arms', in accordance with the proposed structure. The ¹H NMR provided a 3:2 ratio for S-methyl and methylene proton resonances at 1.76 (s) and 4.08 (d, $J_{PH} = 11.9$ Hz) ppm. Of all the compounds presented here, only the cations 5 and 6 provided useful FAB mass spectrometric data. The molecular ion observed in the FAB mass spectrum of complex 6 at m/z = 1338 supports the proposed composition, as do the microanalytical data. This is the first time that all three gold atoms of a trigold(trisphosphine) complex have been coordinated to a single sulfur atom.

Structural Discussion

Crystals of compound **5**, grown by diffusion of pentane into a dichloromethane solution of the com-



Fig. 1. Molecular structure of the cation in crystals of 5 \times CH_2Cl_2 \times 1.5 H_2O.

plex (no exclusion of air humidity), are triclinic, space group $P\overline{1}$, with Z = 2 formula units in the unit cell, together with two CH₂Cl₂ solvent molecules and three molecules of water, one of which is disordered. The anions and cations are well separated with no conspicuous sub-van-der Waals contacts.

The structure of the cation is shown in Fig. 1. The three gold atoms are all positioned on one side of the trifunctional arene ligand. Each phosphorus atom bears one gold atom, and two methylthiolate groups are in bridging position between these gold atoms. Thus S1 is connecting Au2 and Au3, while S2 is connecting Au1 and Au3. Au3 is therefore three-coordinate, while Au1 and Au2 are two-coordinate. The angle Au1-S2-Au3 is very small [81.7(1)°] which brings the two gold atoms rather close together [Au1-Au3 3.1357(9) Å] suggesting aurophilic bonding. The angle Au2-S1-Au3 [98.1(1)°] is larger which leads to a much longer contact Au2-Au3 = 3.645(1) Å, already at the limit of significant metal-metal interactions.

Both sulfur atoms are in a pyramidal configuration with sums of their three angles at 316.6 (S1) and 290.6° (S2), respectively. The methyl group at S1 is oriented towards the center of the complex, but that at S2 is pointing towards the periphery avoiding a steric conflict.

If the unsymmetrical structure of the cation is retained in solution, it would require three inequivalent phosphorus atoms to be detected in the NMR spectrum, and the three methyl groups of the central



Fig. 2. Atomic numbering of all non-hydrogen atoms in the cation of **5**.

arene ring should also be inequivalent, as should be the two methylthiolate groups etc. The room temperature spectra of compound **5** show equivalence of these atoms and groups, however, suggesting a fluxional behaviour rendering the atoms equivalent on the NMR time-scale. Low temperature spectra (to -60°C) did not give the expected full resolution, probably because some of the intramolecular motions are still not sufficiently slow under these conditions.

There is precedence for this type of fluxionality, even for closely related cases with two thiolate ligands bridging three gold atoms. Compound **5** is the only case, however, where the terdentate ligand has potential threefold symmetry.

Conclusion

As a result of both pharmacological application and academic interest, (phosphine)gold(I) thiolate chemistry has been widely investigated. The use of tris(phosphines), however, has been less well explored and this work demonstrates how a tris(phosphine) base can be designed in order to serve as a platform for the mutual interaction of several gold centers. This provides an indication of the way in which patterns of even more complex aggregates based on polydentate donors can be achieved.

Experimental Section

General Information. The experiments were carried out routinely in air. NMR: JEOL GX 400 spectrometer using deuterated solvents with the usual standards at 25 °C. The species HSC_6H_4Me-4 , KSCN, NaSMe, 4mercaptoquinoline, sodium sulfide and AgOTf were obtained commercially. The phosphine ligand, 1,3,5-tris-[(diphenylphosphanylmethyl)trimethylbenzene] (P₃) was prepared following the procedure reported by Aguiar and Daigle [21]. The species [ClAu(tht)] (tht = tetrahydrothiophene) [22] and [ClAu(SMe₂)] [23] were synthesized according to the literature methods.

$[(P_3)(AuCl)_3](1)$

A solution of P_3 (1.43 g, 2.00 mmol) in dichloromethane (100 ml) was added dropwise to a stirred solution of [ClAu(SMe₂)] (1.77 g, 6.00 mmol) in dichloromethane (50 ml). After stirring for 2 h, the solvent volume was reduced to ca. 20 ml and pentane (60 ml) added to precipitate the colorless product. Yield: 95% (2.86 g). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): 29.9 (s) ppm. ¹H NMR (CDCl₃): 1.78 (s, 9 H, CH₃), 3.84 (d, 6 H, CH₂, $J_{PH} = 13.0$ Hz), 7.43 - 7.67 (m, 30 H, C₆H₅) ppm. ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): 135.8 (m, $C^{2,4,6}C_6Me_3$), 133.6 (d, $o/m-C_6H_5$, $J_{CP} = 13.0$ Hz), 132.2 (s, $p-C_6H_5$), 131.0 (m, $C^{1,3,5}C_6Me_3$), 129.6 (d, *ipso-C*₆H₅, J_{CP} = 61.0 Hz), 128.4 (d, $o/m-C_6H_5$, $J_{CP} = 13.0$ Hz), 31.8 (d, CH_2 , $J_{CP} = 23.0$ Hz), 20.3 (s, CH_3) ppm. Analysis for C₄₈H₄₅Au₃Cl₃P₃ · 3 CH₂Cl₂: calcd. C 36.75, H 3.08; found C 36.33, H 3.13. The dichloromethane tris-solvate was confirmed by integration of the ¹H NMR spectrum.

$[(P_3)(AuSCN)_3](2)$

A methanolic solution (10 ml) of KSCN (21 mg, 0.071 mmol) was added to a stirred solution of [(P₃)(AuCl)₃] (1) (100 mg, 0.071 mmol) in dichloromethane (25 ml). After stirring for 1 h, the solution was filtered through diatomaceous earth to remove precipitated KCl. Ethanol (10 ml) was added and the solvent volume reduced to precipitate the colorless product in 57% (60 mg) yield. The product is slightly soluble in ethanol, however this provides better quality crystals than precipitation with pentane. ³¹P{¹H} NMR (CDCl₃): 36.9 (s) ppm. ¹H NMR (CD₂Cl₂): 1.82 (s, 9 H, CH₃), 3.98 (d, 6 H, CH₂, $J_{PH} = 12.1$ Hz), 7.51 - 7.75 (m \times 2, 30 H, C₆H₅) ppm. Analysis for C₅₁H₄₅Au₃N₃P₃S₃ \cdot CH₂Cl₂: calcd. C 39.91, H 3.01, N 2.69; found C 39.68, H 3.01, N 2.31. The monodichloromethane solvate was confirmed by integration of the ¹H NMR spectrum.

$[(P_3)(AuSC_6H_4Me-4)_3]$ (3)

 $[(P_3)(AuCl)_3]$ (1) (100 mg, 0.071 mmol) and HSC_6H_4Me -4 (30 mg, 0.242 mmol) were dissolved in dichloromethane (20 ml) and a methanolic solution (5 ml)

of NaOMe (13 mg, 0.241 mmol) added. After stirring for 1 h, the solution was filtered through diatomaceous earth to remove precipitated NaCl. Diethyl ether (25 ml) was added to precipitate the colorless product in 70% (83 mg) yield. ³¹P{¹H} NMR (CDCl₃): 35.0 (s) ppm. ¹H NMR (CDCl₃): 1.76 (s, 9 H, CH₃), 2.43 (s, 9 H, tolyl-CH₃), 3.74 (d, 6 H, CH₂, $J_{PH} = 10.6$ Hz), 6.89, 7.08 (AB system, 12 H, C₆H₄, $J_{HH} = 8.1$ Hz), 7.46, 7.68 (m, 30 H, C₆H₅) ppm. Analysis for C₆₉H₆₆Au₃P₃S₃: calcd. C 49.47, H 3.97; found C 49.20, H 3.96.

$[(P_3)(AuSQn)_3]$ (4)

A methanolic solution (10 ml) of HSQn (34 mg, 0.211 mmol) and NaOMe (13 mg, 0.241 mmol) was added to a stirred solution of $[(P_3)(AuCl)_3]$ (1) (100 mg, 0.071 mmol) in dichloromethane (25 ml). After stirring for 1 h, the solution was filtered through diatomaceous earth to remove precipitated NaCl. Pentane (25 ml) was added to precipitate the colorless product in 64% (81 mg) yield. ³¹P{¹H} NMR (CDCl_3): 34.5 ppm. ¹H NMR (CDCl_3): 1.80 (s, 9 H, CH_3), 3.68 (d, 6 H, CH₂, $J_{PH} = 7.4$ Hz), 7.26 - 7.82 (m, 51 H, C₆H₅ + SQn) ppm. Analysis for C₇₈H₆₆Au₃P₃S₃ · 2 CH₂Cl₂: calcd. C 49.19, H 3.61; found C 48.56, H 3.86.

$[(P_3)Au_3(SMe)_2]Cl(5)$

An aqueous solution (5 ml) of NaSMe (10 mg, 0.143 mmol) was added to a stirred solution of $[(P_3)(AuCl)_3]$ (1) (100 mg, 0.071 mmol) in acetone (30 ml). After stirring for 1 h, all solvent was removed. The crude product was redissolved in dichloromethane (20 ml) and filtered through diatomaceous earth to remove precipitated NaCl. Pentane (20 ml) was added to precipitate the colorless product in 63% (62 mg) yield. MS (FAB) m/z = 1399, 100% [M]⁺. ³¹P{¹H} NMR (CD₂Cl₂): 34.6 [s(br)] ppm.¹H NMR (CD₂Cl₂): 1.76 (s, 9 H, CCH₃), 2.53 (s, 6 H, SCH₃) 4.01 (d, 6 H, CH₂, $J_{PH} = 12.1$ Hz), 7.48 - 7.85 (m, 30 H, C₆H₅) ppm. Analysis for C₅₀H₅₁Au₃ClP₃S₂: calcd. C 41.83, H 3.56; found C 41.31, H 3.80.

$[(P_3)Au_3S]BF_4/OTf(6)$

a) $[(P_3)(AuCl)_3]$ (1) (74 mg, 0.05 mmol) and AgOSO₂CF₃ (41 mg, 0.16 mmol) were stirred in tetrahydrofuran (30 ml) for 10 min at 0°C. This solution was filtered through diatomaceous earth into a tetrahydrofuran (10 ml) solution of Na₂S · 9 H₂O (25 mg, 0.10 mmol). After stirring for 2 h, all solvent was removed and the crude product redissolved in dichloromethane (20 ml) and again filtered through diatomaceous earth. The

solvent volume was reduced to ca. 5 ml and pentane (20 ml) added to precipitate the colorless product in 78% $(61 \text{ mg}) \text{ yield. } \mathbf{b} [(P_3)(AuCl)_3] (1) (100 \text{ mg}, 0.071 \text{ mmol})$ was dissolved in dichloromethane (20 ml) and an aqueous (15 ml) mixture of Na₂S · 9 H₂O (50 mg, 0.21 mmol) and NaBF₄ (30 mg, 0.27 mmol) was added. The biphasic mixture was stirred for 3 h. The non-aqueous layer was decanted and the aqueous layer washed twice with dichloromethane (10 ml). The extracts were combined and the solvent volume reduced to ca. 5 ml and diethyl ether (20 ml) added to precipitate the colorless product in 62% (63 mg) yield. MS (FAB) m/z = 1338, 66% $[M]^+$. ³¹P{¹H} NMR (CD₂Cl₂): 37.8 (s) ppm.¹H NMR (CD_2Cl_2) : 1.76 (s, 9 H, CCH₃), 4.08 (d, 6 H, CH₂, J_{PH} = 11.9 Hz), 7.51 - 7.95 (m, 30 H, C₆H₅) ppm. Analysis for C49H45Au3F3O3P3S2: calcd. C 39.57, H 3.03; found C 39.68, H 3.30.

X-ray crystallography

A specimen of suitable quality and size of compound 5 was mounted on the end of a quartz fiber in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_{α} radiation. The structure was solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix leastsquares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions.

Crystal data for $C_{51}H_{56}Au_3Cl_3O_{1.5}P_3S_2$: M = 1547.24, triclinic, a = 9.4468(3), b = 13.8460(5), c = 19.9789(9) Å, $\alpha = 86.057(1)$, $\beta = 88.580(2)$, $\gamma = 84.255(4)^{\circ}$, space group $P\bar{1}$, Z = 2, V = 2593.5(2) Å³, T = 148 K, μ (Mo-K_{α}) = 88.29 cm⁻¹, 99208 measured and 9877 unique reflections ($R_{int} = 0.620$), wR2 = 0.1437, R1 = 0.0604 for 9877 reflections [$I \ge 2\sigma$ (I)] and 582 parameters.

Thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-170631.

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