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

James D. E. T. Wilton-Ely, Stefan Hofreiter, Norbert W. Mitzel, and Hubert Schmidbaur

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

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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 (HSC₉H₄Me-4) and 2-mercaptoquinoline (2-HSQn) to provide the complexes [(P₃)(AuSC₉H₄Me-4)] and [(P₃)(AuSQn)]₃, respectively. Reaction of [(P₃)(AuCl)] 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)] and AgOTf) and sodium sulfide yields the complex [(P₃)Au₃S]OSO₂CF₃, the first example of a trigoldsulfonium unit coordinated to a tridentate phosphate. The tetrafluoroborate salt is obtained from [(P₃)(AuCl)] and Na₂S - 9 H₂O in the presence of NaBF₄. The structure of [(P₃)(AuMeS)₃]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[AuPPPh₃]ₙ⁺ in 1980 [5], which are analogues of the corresponding complexes of the heavier chalcogen elements A[AuPPh₃]ₙ⁺ (A = S, Se, Te [6, 7]). These thrici aurated complexes are among the best-known 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 phosphate ligands has been the subject of a number of reports. The tris[2-(diphenylphosphino)ethyl]amine ligand (NP₃) was found to react with [LAuCl] (L = tetrahydrothiophene, PPh₃) to give the cations [Au(NP₃)]⁺X⁻ (X = Cl⁻, PF₆⁻, NO₃⁻, Scheme 1, a) for which X-ray structures (of the PF₆⁻ and NO₃⁻ salts) were established [9]. It was discovered that if BPh₃ 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 phosphate ‘arm’ reaches across to bind to the second gold center (Scheme 1, b). The complexes ClAuP(C₂H₅)₃nPPh₂AuCl₂ (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 [PF₃PCH₂P(Ph)CH₂PPh₂]₂Au₃(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 [PhClAuP(C₆H₄P(AuCl)Ph₂-2)]₂ (Scheme 1, e) from the tridentate phosphate [PhP(C₆H₄PPh₂-2)]₂.
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 [Au_2(tppm)(AuCl)](ClO_4)_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 [Au_2] 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 (P_3), 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[(diphenylphosphanyl)methyl]trimethylbenzene (P_3) was found to react cleanly with three molar equivalents of either (tht)AuCl or (Me_2S)AuCl to provide the desired trigold complex [(P_3)(AuCl)_3] (I) 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_{P-H} = 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, 6Q Me_3) and 131.0 (C_1,3,5Q Me_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_{P-C} = 23.0 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-
Scheme 2. Preparation of the complexes. (i) 3[(Me_2S)AuCl]; (ii) 3KSCN; (iii) 3HSTol (Tol = C_6H_4Me-4), 3NaOMe; (iv) 3HSQn (Qn = quinoline), 3NaOMe; (v) 2 - 10 mol. eq. NaSMe (vi) 3AgOTf, Na_2S.

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

did not provide the expected 2:3 ratio of methylen to S-methyl protons expected for a product of composition [(P_3)(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_2(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 [C_6H_4(CH_2PPh_2)AuSMe]_2-1,4 and [C_6H_4-(1,4-CH_2PPh_2)AuSMe]BF_4 have been prepared from [C_6H_4(CH_2PPh_2)PAuCl]_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 $P_3$ ligand compared to the related 1,4,4-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$_2$CF$_3$ 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$_2$S • 9 H$_2$O 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 $^{31}$P 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 $^1$H 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 $m/z = 1388$ 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 complex (no exclusion of air humidity), are triclinic, space group $P1$, with $Z = 2$ formula units in the unit cell, together with two CH$_2$Cl$_2$ 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
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 HSC₆H₄Me₄, KSCN, NaSMe, 4-mercaptopyridine, 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.

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[(P₃)(AuCl)]_3 \quad (1)
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A solution of P₃ (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). \[^{31}P \{^1H\} NMR (CDCl₃): 29.9 (s) ppm. \]

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^1H NMR (CDCl₃): 1.78 (s, 9 H, CH₃), 3.84 (d, 6 H, CH₂, \(J_{HH} = 13.0 \) Hz), 7.43 - 7.67 (m, 30 H, C₆H₅) ppm. \[^{13}C \{^1H\} NMR (CDCl₃): 135.8 (m, C\{2,4,6\}C₆H₅), 133.6 (d, \(o/m-C\{6\}C₆H₅, J_{CP} = 13.0 \) Hz), 132.2 (s, \(p-C\{6\}C₆H₅) ppm. Analysis for C\{13\}H\{25\}AuCl₂P₃ \cdot 3 CH₂Cl₂: calc. 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.

\[
[(P₃)(AuSCN)]₃ \quad (2)
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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. \[^{31}P \{^1H\} NMR (CDCl₃): 36.9 (s) ppm. \]

\[^1H NMR (CDCl₃): 1.82 (s, 9 H, CH₃), 3.98 \]

(d, 6 H, CH₂, \(J_{HH} = 12.1 \) Hz), 7.51 - 7.75 (m, 2 × 30 H, C₆H₅) ppm. Analysis for C\{25\}H\{45\}Au₃S₃P₃S₃ \cdot CH₂Cl₂: calc. 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.

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[(P₃)(AuSC₆H₄Me₄)]_3 \quad (3)
\]

[(P₃)(AuCl)]₃ (1) (100 mg, 0.071 mmol) and HSC₆H₄Me₄ (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 78% (61 mg) yield. \(^{31}P\left({^1}H\right)\) NMR (CDCl\(_3\)): 35.0 (s) ppm. \(^1\)H NMR (CDCl\(_3\)): 1.76 (s, 9 H, CH\(_3\)), 2.43 (s, 9 H, tolyl-CH\(_3\)), 3.74 (d, 6 H, CH\(_2\), \(J_{PH} = 10.6\) Hz), 6.89, 7.08 (AB system, 12 H, C\(_6\)H\(_5\)), \(J_{HH} = 8.1\) Hz), 7.46, 7.68 (m, 30 H, C\(_6\)H\(_5\)) ppm. Analysis for C\(_{90}H_{65}Au_3P_5S_3\): calcd. C 49.47, H 3.97; found C 49.20, H 3.96.

\([\{(P_3)(Au(SQn)_3)\}]\) (4)

A methanolic solution (10 ml) of HSO\(_4\)N (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% (62 mg) yield. MS (FAB) \(m/z = 1399, 100\% \text{[M]}^{+}\). \(^{31}P\left({^1}H\right)\) NMR (CDCl\(_3\)): 34.5 ppm. \(^1\)H NMR (CDCl\(_3\)): 1.80 (s, 9 H, CH\(_3\)), 3.68 (d, 6 H, CH\(_2\), \(J_{PH} = 7.4\) Hz), 7.26 - 7.82 (m, 51 H, C\(_6\)H\(_5\)) ppm. Analysis for C\(_{78}H_{68}Au_3P_5S_3\): calcd. C 48.56, H 3.86.

\([\{(P_3)(Au(SMe)_2)_2\}]\)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% (63 mg) yield. MS (FAB) \(m/z = 1399, 100\% \text{[M]}^{+}\). \(^{31}P\left({^1}H\right)\) NMR (CDCl\(_3\)): 34.6 [s(br)] ppm. \(^1\)H NMR (CDCl\(_3\)): 1.76 (s, 9 H, CCH\(_3\)), 2.53 (s, 6 H, C\(_6\)H\(_5\)), 4.01 (d, 6 H, CH\(_2\), \(J_{PH} = 11.9\) Hz), 7.51 - 7.95 (m, 30 H, C\(_6\)H\(_5\)) ppm. Analysis for C\(_{78}H_{68}Au_3P_5S_3\): calcd. C 49.19, H 3.61; found C 48.56, H 3.86.

\([\{(P_3)(AuCl)_3\}]\) (1) (74 mg, 0.05 mmol) and AgOSO\(_3\)CF\(_3\) (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 Na\(_2\)S \(\cdot\) 9 H\(_2\)O (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 mg) yield. \([\{(P_3)(AuCl)_3\}]\) (1) (100 mg, 0.071 mmol) was dissolved in dichloromethane (20 ml) and an aqueous (15 ml) mixture of Na\(_2\)S \(\cdot\) 9 H\(_2\)O (50 mg, 0.21 mmol) and NaBF\(_4\) (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) \(m/z = 1338, 66\% \text{[M]}^{+}\). \(^{31}P\left({^1}H\right)\) NMR (CDCl\(_3\)): 37.8 (s) ppm. \(^1\)H NMR (CDCl\(_3\)): 1.76 (s, 9 H, CCH\(_3\)), 4.08 (d, 6 H, CH\(_2\), \(J_{PH} = 11.9\) Hz), 7.51 - 7.95 (m, 30 H, C\(_6\)H\(_5\)) ppm. Analysis for C\(_{90}H_{65}Au_3P_5S_3\): 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\(_\alpha\) radiation. The structure was solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares 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\(_{50}H_{55}Au_3Cl_3O_2\)P_5S_3:** \(M = 1547.24\), triclinic, \(a = 9.4468(3), b = 13.8460(5), c = 19.9789(9)\) \(\AA\). \(\alpha = 86.057(1), \beta = 88.580(2), \gamma = 84.255(4)\)°, space group \(P\bar{1}\), \(Z = 2, V = 2593.5(2)\) \(\AA^3\), \(T = 148\) K, \(\mu(Mo-K\_\alpha) = 88.29\) cm\(^{-1}\), 99208 measured and 9877 unique reflections \((R_{int} = 0.620), wR = 0.1437, R = 0.0604\) for 9877 reflections \([I \geq 2\sigma (I)]\) 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 CCDC-170631.

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