

The Supramolecular Structures of Complex Tri[gold(I)]sulfonium Cations

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Supramolecular aggregation

Tris[(trimethylphosphane)gold(I)]sulfonium tetrafluoroborate (**1**) has been prepared from the corresponding oxonium salt $[(\text{Me}_3\text{P})\text{Au}]_3\text{O}^+ \text{BF}_4^-$ and bis(trimethylsilyl) sulfide, $(\text{Me}_3\text{Si})_2\text{S}$. The analogous triisopropylphosphane and methyl-diphenylphosphane complexes (**2**, **3**) have been obtained in a similar way. The products are stable crystalline solids, the structure of which has been determined by X-ray methods. They are composed of independent tetrafluoroborate anions and pyramidal tri(gold)sulfonium cations, which are aggregated to form dimeric units (as in **3**) or even strings of dimers (as in

1). It is only in complex **2** that steric effects, originating from the bulky phosphane ligands, prevent the building of supramolecular (supracationic) aggregates. In the independent pyramidal cations of **2** only short *intracationic* Au...Au contacts have been detected. These are complemented by *intercationic* gold-gold contacts of similar length in the structures of **1** and **3**. – In the preparation of complex **1**, the species $[(\text{Me}_3\text{P})\text{Au}]_4\text{S}^{2+} (\text{BF}_4^-)_2$ (**4**) with hypercoordinate sulfur atoms has also been detected by mass spectroscopy.

Gold(I) complexes have a very unusual structural chemistry based on non-classical intermolecular gold-gold contacts^[1]. Many two-coordinate coordination compounds of the type L–Au–X have been found to form supramolecular aggregates with Au...Au distances^[2] of ca. 3.0 Å associated with bond energies^[3] of ca. 8 kcal/mol. This secondary bonding represents weak forces between the closed-shell metal atoms (Au^1 : $5d^{10}$) originating from significant changes in the energy characteristics of the valence electrons of gold by *relativistic effects*^[1,4]. In the Periodic Table these effects reach a local maximum for gold in the heavy element region^[5].

The stabilisation of molecular systems associated with this type of bonding is particularly strong in polynuclear species, where gold atoms can cluster in small aggregates, either in a homo- or heteroatomic way^[1,6]. Element-centered gold(I) clusters of hypercoordinate carbon, nitrogen, and phosphorus are among the most striking examples for this new type of aggregation^[7]. For *sulfur*, the chemistry of gold(I) clusters of this type was originally^[8] limited to the *trigoldsulfonium* cations of the type $[(\text{LAu})_3\text{S}]^+$, but very recently this class of compounds could also be extended^[9] to include the first *tetragoldsulfodionium* cation $[(\text{LAu})_4\text{S}]^{2+}$ isoelectronic and isostructural with the corresponding phosphonium^[10] and arsonium^[11] cations $[(\text{LAu})_4\text{E}]^+$.

The strength of the Au...Au interactions is influenced also by the electronic effects of the substituents L and X at gold, and some experimental findings^[2b] as well as theoretical calculations^[12] have indicated that soft ligands of low group electronegativity should shorten the Au–Au distance and increase the bond energy. More recent data have shown, however, that even within the series with X = hal-

ogen the results are not consistent with this simple picture^[13]. On the other hand, it is becoming more and more obvious that steric effects are playing a decisive role, since the weak forces associated with the Au...Au contacts are easily overruled by steric repulsion and other components such as packing forces^[14]. (In solution, it is the solvation by solvent molecules which is overruling the aggregation by Au...Au contacts.)

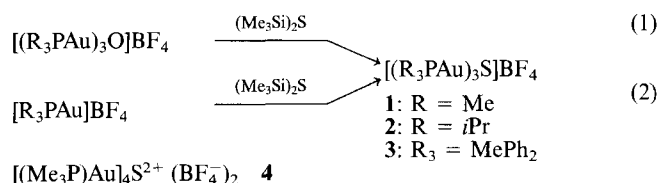
The present study was undertaken in order to contribute to the open questions regarding the supramolecular aggregation of sulfur-centered gold cluster cations $[(\text{R}_3\text{P})\text{Au}]_3\text{S}^+$ by changing more systematically the size and electronic/inductive effects of the ligands.

Gold thiolates – with or without stabilizing phosphane ligands – are of great value for a large number of applications, as exemplified by the central role of (phosphane)-gold thiolates $\text{R}_3\text{PAuSR}'$ in gold therapy^[15] and of a variety of RSAu species in the pastes designated as “liquid gold” for gilding^[16]. Gold/thiol interfaces are among the most useful model systems in surface science^[17]. Finally, labeling of biochemical substrates by heavy elements like gold at sulfur centers is important for many methods of biondiagnostics^[18].

Preparation and Characterization of the Compounds

The tris[(triorganophosphane)gold(I)]sulfonium salts are available according to two reaction pathways starting either from the oxonium analogues $[(\text{R}_3\text{P})\text{Au}]_3\text{O}^+$ or from (triorganophosphane)gold(I) tetrafluoroborates (prepared *in situ*) with bis(trimethylsilyl) sulfide [Eq. (1,2)]. In earlier work hydrogen sulfide^[8a] and other sulfides have also been used (instead of the silyl sulfide), but the route via the (liquid) silicon compound proved to be the easier method,

as already shown in very early studies on the selenium analogue^[19].



The products are obtained as colorless or pale yellow crystalline solids in acceptable yields. The compounds **1–3** are stable in air for short periods of time. They are soluble in halocarbon and other polar organic solvents. These solutions show the expected set of NMR signals for the tertiary phosphane ligands and for the tetrafluoroborate counterion. In the mass spectra the parent cations are observed in high intensity (see Experimental). All three compounds show strong photoluminescence upon UV photoexcitation typical and diagnostic of gold(I) cluster species^[20].

Crystal and Molecular Structures of the Compounds

The structure of compound **2** with its bulky isopropyl substituents is ionic with monomeric tri(gold)sulfonium cations and tetrafluoroborate anions. The asymmetric unit contains 1/3 of the cation, which has threefold symmetry (Figure 1). The Au–Au distances of 3.253(1) Å and uncompressed angles Au–S–Au of 90.8(4)° are indicative of steric repulsion associated with the bulky tertiary phosphanes. With smaller phosphanes the metal–metal distances in this type of compounds are shorter and the Au–S–Au angles are smaller than 90° (below). The Au–P and Au–S distances are within the range of standard distances of (phosphane)gold(I) thiolates. The crystal lattice contains no solvent, and there are no unusual contacts between cations and anions. The anions are disordered, but the atomic coordinates could be accounted for by a split model.

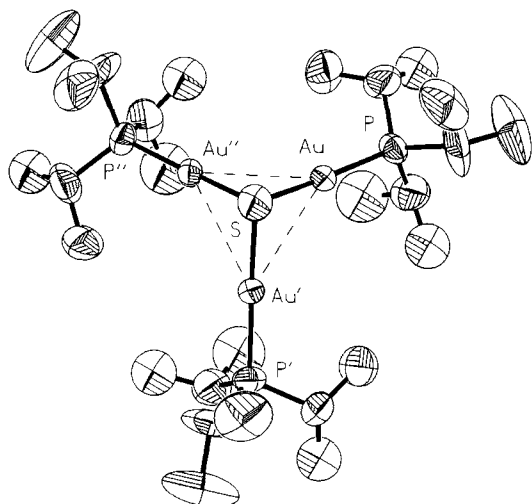


Figure 1. Molecular structure of the cation $[(iPr)_3PAu]_3S^+$ in the tetrafluoroborate salt **2** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). A threefold axis passes through the sulfur atom. Selected bond distances [Å] and angles [°]: Au–S 2.285(8), Au–P 2.240(3), Au–Au' 3.253(1), Au–S–Au' 90.8(4), P–Au–S 169.9(3)

Compound **3** crystallizes with one tri(gold)sulfonium cation, one tetrafluoroborate anion, and one dichloromethane solvent molecule in the unit cell. (The solvent molecules are disordered.) The cations of neighboring units are associated into dimers, however, which have a crystallographic center of inversion (Figure 2). The three Au–Au contacts of a monomeric unit are showing considerable differences in length [Au1–Au2 3.228(1), Au1–Au3 2.990(1), Au2–Au3 3.008(1) Å], but are generally much shorter than in complex **2** (above). Accordingly, the angles at sulfur are all smaller than 90° [Au1–S–Au2 87.5(1), Au1–S–Au3 79.5(1), Au2–S–Au3 79.7(1)°]. The gold–gold contacts between the monomers are also short at 3.055(1) Å, a value close to the average of the internal contacts in the monomeric unit. There is thus little difference between *intra*- and *inter* cationic Au–Au interactions. The overall structure is similar to that of the triphenylphosphane complex in the hexafluorophosphate^[8c]. Clearly, the steric and electronic effects of these ligands are very similar and have the same structural consequences. It should be remembered, however, that the nature of the anion may also play a significant role: The cation $[(Ph_3P)Au]_3S^+$ is a *monomer* in the tetrafluoroborate salt^[8d], but a dimer in the hexafluorophosphate!

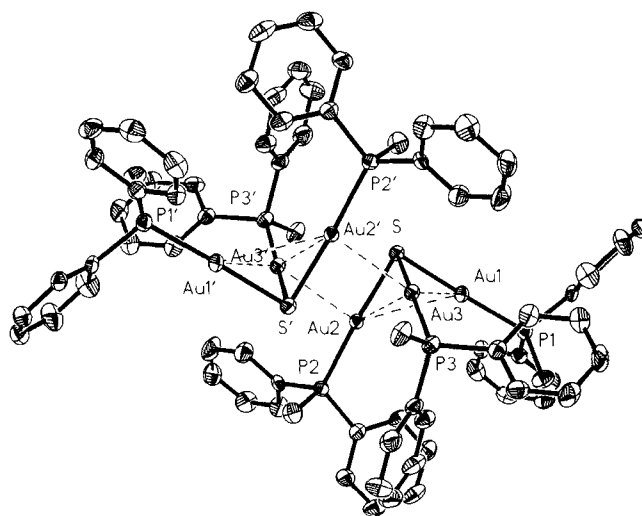


Figure 2. Molecular structure of a pair of cations $[(MePh_2P)Au]_3S^+$ in the tetrafluoroborate salt **3** · CH₂Cl₂ (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). The monomers are related to each other by a center of inversion. Selected bond distances [Å] and angles [°]: S–Au1 2.326(2), S–Au2 2.343(2), S–Au3 2.352(2), Au1–P1 2.258(2), Au2–P2 2.267(2), Au3–P3 2.263(3), Au1–Au2 3.228(1), Au2–Au3 3.008(1), Au1–Au3 2.990(1), Au2–Au3' 3.055(1), S–Au1–P1 178.0(1), S–Au2–P2 177.0(1), S–Au3–P3 170.2(1), Au1–S–Au2 87.5(1), Au2–S–Au3 79.7(1), Au1–S–Au3 79.5(1)

Complex **1** forms triclinic crystals, space group $P\bar{1}$ with two independent formula units (A and B) and three molecules of the dichloromethane solvent in the asymmetric unit. The sulfonium cations are both forming pairs (dimers A₂ and B₂), each with a crystallographic center of inversion (Figure 3). These dimers are aggregated further into strings of dimers (–A–A–B–B–) with short gold–gold contacts (A–B) as links (Figure 4). The supramolecular contact Au1–Au6 between units A and B (two half dimers) is

shown in Figure 5. The Au–Au distances are found in the range from 3.034(1) to 3.420(1) Å for both the intra- and intercationic contacts, which are quite similar, as also found for **3**. The Au–S–Au angles cover a broad range [between 80.8(1) and 94.4(1)°] with some of them as much as 10° smaller than the 90° reference for tricoordinate sulfonium centers. Clearly, the Au–Au contacts constrain the Au₃ triangles in each of the cations. The Au–S distances are similar to those found in the dimers of **3**, but larger than in the monomers of **2**, indicating that the aggregation of compounds with smaller tertiary phosphanes leads to a lengthening of the Au–S bonds, but also to a shortening of the Au–Au contacts and a decrease of the Au–S–Au angles.

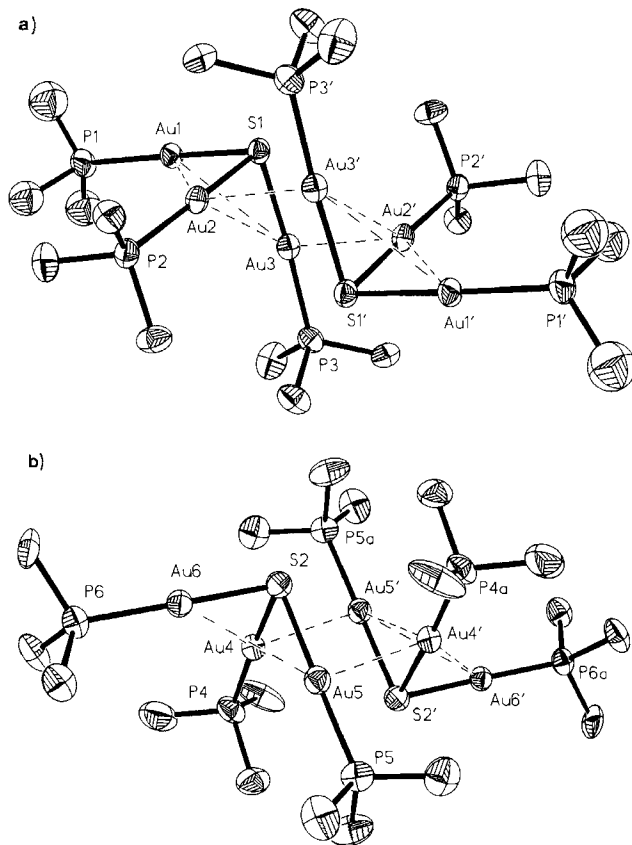


Figure 3. a) A pair of cations $[(\text{Me}_3\text{P})\text{Au}]_3\text{S}^+$ (A_2 , see text) in the tetrafluoroborate salt $\mathbf{1} \cdot 1.5 \text{CH}_2\text{Cl}_2$ (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). The dimer has a center of inversion. Selected bond distances [Å] and angles [°]: S1–Au1 2.332(4), S1–Au2 2.354(3), S1–Au3 2.331(4), Au1–P1 2.260(4), Au2–P2 2.268(4), Au3–P3 2.266(5), Au1–Au2 3.060(1), Au1–Au3 3.420(1), Au2–Au3 3.176(1), Au2–Au3' 3.109(1), S1–Au1–P1 172.6(2), S1–Au2–P2 176.5(1), S1–Au3–P3 176.9(1). – b) Cation pair B_2 (see text) of compound $\mathbf{1} \cdot 1.5 \text{CH}_2\text{Cl}_2$ [see a) for details]. The dimer has a center of inversion. Selected bond distances [Å] and angles [°]: S2–Au4 2.341(4), S2–Au5 2.339(4), S2–Au6 2.311(5), Au4–P4 2.254(4), Au5–P5 2.256(4), Au6–P6 2.241(5), Au4–Au5 3.034(1), Au4–Au6 3.213(1), Au5–Au6 3.347(1), Au4–Au5' 3.045(1), S2–Au4–P4 174.2(2), S2–Au5–P5 178.9(2), S2–Au6–P6 174.6(2).

Discussion

The new results on the supramolecular structure of the tri[gold(I)]sulfonium cations illustrate the versatility in the aggregation pattern for element-centered gold clusters. At

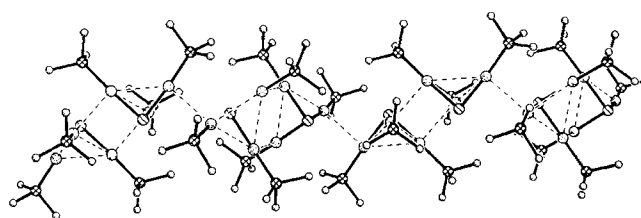


Figure 4. A chain of $[(\text{Me}_3\text{P})\text{Au}]_3\text{S}^+$ cations in the lattice of $\mathbf{1} \cdot 1.5 \text{CH}_2\text{Cl}_2$. The sequence of the units is –A–A–B–B– (see Figure 3). Gold, sulfur, and phosphorus atoms are drawn with different shadings, carbon atoms are small white circles, hydrogen atoms have been omitted

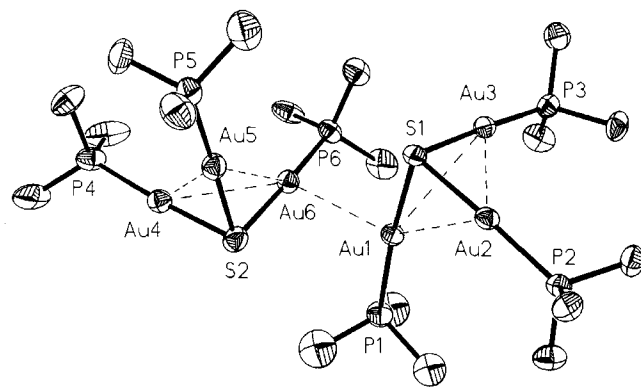


Figure 5. Pair of crystallographically non-equivalent cations $[(\text{Me}_3\text{P})\text{Au}]_3\text{S}^+$ (AB, see text) of compound $\mathbf{1} \cdot 1.5 \text{CH}_2\text{Cl}_2$. This unit is a detail of the chain represented in Figure 4. The connection is through the Au1–Au6 contact: 3.077(1) Å. The other dimensions are listed in the caption to Figure 3

this stage it is not yet obvious, which of the many factors involved ultimately decides on the nature of the association of the individual units. The differences between the structures of the oxonium^[21] and sulfonium^[8] species with the same ligands $L = \text{R}_3\text{P}$ are examples. For sulfur and PMe_3 , the $\text{S}(\text{AuL})_3$ pyramids are grouped in pairs through two new Au–Au contacts, which are further linked by Au–Au single contacts to give strings. For oxygen and PMe_3 , however, the pairs of $\text{O}(\text{AuL})_3$ pyramids are formed by a more intimate clustering which gives rise to four new Au–Au contacts^[21].

While there can be no question that it is the Au–Au contact formation which determines the aggregation, the stereochemistry of the intercationic approach and the number of metal-metal contacts are codetermined by other factors. Steric hindrance appears to be a major component, but electronic influences cannot be neglected. Presently, the latter are the least understood, and there is even conflicting evidence from theory and experiment^[2b,2f,12,13,21]. Further work now in progress is hoped to answer some of the open questions.

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Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves in a nitrogen atmosphere. — NMR: CDCl₃ as solvent, TMS as internal standard for ¹H and ¹³C{¹H}, H₃PO₄ (85%) as external standard for ³¹P{¹H}, Jeol GX 270, Jeol GX 400. — MS: Varian MAT 90.

Tris[(trimethylphosphane)gold(I)]sulfonium Tetrafluoroborate (1): To a solution of [(Me₃PAu)₃O]BF₄^[21] (190 mg, 0.21 mmol) in dichloromethane (15 ml) a solution of S(SiMe₃)₂ (0.045 ml, 0.21 mmol) in dichloromethane (10 ml) was added dropwise at room temp. and allowed to react for 3 h with stirring at room temp. to give a yellow solution. After the volume of the solution had been reduced to 15 ml in vacuo, diethyl ether was added to precipitate the solids. Pure, crystalline product was obtained from a dichloromethane solution by slowly removing the solvent. **1**, faint yellow crystals (from dichloromethane), yield 95 mg (48%), dec. temp. 175°C. — C₃₉H₂₇Au₃BF₄P₃S (938.0): calcd. C 11.52, H 2.90, S 3.42; found C 12.00, H 3.18, S 3.66. — ¹H NMR: δ = 1.6 [d, J(PH) = 10.7 Hz]. — ¹³C{¹H} NMR: δ = 16.1 [d, J(PC) = 37.7 Hz]. — ³¹P{¹H} NMR: δ = -3.9. — MS (FAB), m/z: 851 (100%).

Tris[(triisopropylphosphane)gold(I)]sulfonium Tetrafluoroborate (2): The reaction was carried out analogously to that described above using 0.06 ml (0.28 mmol) of S(SiMe₃)₂ and 330 mg (0.28 mmol) of [(iPr₃PAu)₃O]BF₄^[22] in 30 ml of CH₂Cl₂. Pure crystalline product **2** was obtained by carefully adding diethyl ether to a dichloromethane solution; yield 330 mg (99%), dec. temp. 221°C. — C₂₇H₆₃Au₃BF₄P₃S (1190.4): calcd. C 27.24, H 5.30, S 2.69; found C 27.82, H 5.53, S 1.83. — ¹H NMR: δ = 1.2 [CH₃, dd, J(PH) = 16.5, J(HH) = 7.3 Hz], 2.2 [CH, dq, J(PH) = 14.5, J(HH) = 7.3 Hz]. — ¹³C{¹H} NMR: δ = 20.2 [CH₃, qdd, J(CH) = 128.7, J(CH) = 5.5, J(PC) = 5.5 Hz], 23.7 [CH, dd, J(CH) = 129.6, J(PC) = 33.1 Hz]. — ³¹P{¹H} NMR: δ = 76.0. — MS (FAB), m/z: 1103 (42%).

Tris[(methylphenylphosphane)gold(I)]sulfonium Tetrafluoroborate (3): A solution of 0.05 ml (0.23 mmol) of S(SiMe₃)₂ in 10 ml of CH₂Cl₂ was added dropwise to a solution of [(Ph₂MeP)Au]BF₄ [freshly prepared from 300 mg (0.69 mmol) of (Ph₂MeP)AuCl^[23] and 134 mg (0.69 mmol) of AgBF₄] in 20 ml of THF at 0°C. After stirring for 4 h the solvent was evaporated in vacuo. The crude product was purified by crystallization from CH₂Cl₂/Et₂O. **3**, yield 285 mg (95%), dec. temp. 160°C. — C₃₉H₃₉Au₃BF₄P₃S (1310.4): calcd. C 35.74, H 2.99, S 2.45; found C 34.76, H 2.94, S 2.49. — ¹H NMR: δ = 1.9 [CH₃, d, J(PP) = 10.4 Hz], 7.2 [H_{3/5}, t, J(HH) = 6.7 Hz], 7.3 [H₄, t, J(HH) = 7.0], 7.5 [H_{2/6}, dd, J(PH) = 12.8, J(HH) = 7.9 Hz]. — ¹³C{¹H} NMR: δ = 14.2 [CH₃, d, J(PC) = 37.7 Hz], 129.3 [C_{3/5}, t, J(PC) = 11.0 Hz], 130.7 [C₁, d, J(PC) = 57.9 Hz], 131.9 (C₄, s), 132.5 [C_{2/6}, d, J(PC) = 13.8 Hz]. — ³¹P{¹H} NMR: δ = 17.9. — MS (FAB), m/z: 1223 (100%).

Tetrakis[(trimethylphosphane)gold(I)]sulfodionium Bis(tetrafluoroborate) (4): Obtained as a byproduct in the preparation of **1**. — MS (FD), m/z: 562 (100%).

X-Ray Structure Determinations: All samples were mounted in glass capillaries. Graphite-monochromated Mo-K_α radiation was used. The structures were solved by direct methods (program: SHELXTL-PC). Hydrogen atoms of non-disordered groups were included in idealized, fixed positions. The final cell parameters and specific data collection parameters are summarized in Table 1. — Details of the X-ray structure determinations have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the deposit number CSD-58 324.

Table 1. Crystallographic data for compounds **1** · 1.5 CH₂Cl₂, **2**, and **3** · CH₂Cl₂

	1 · 1.5 CH ₂ Cl ₂	2	3 · CH ₂ Cl ₂
Formula	C _{10.5} H ₃₀ Au ₃ P ₃ SBF ₄ Cl ₃	C ₂₇ H ₆₃ Au ₃ P ₃ SBF ₄	C ₄₀ H ₄₁ Au ₃ P ₃ SBF ₄ Cl ₂
Mw	1065.4	1190.4	1395.3
Cryst. system	triclinic	hexagonal	triclinic
Space group	P $\bar{1}$ (No. 2)	R $\bar{3}$ (No. 148)	P $\bar{1}$ (No. 2)
a [Å]	13.220(2)	13.633(1)	12.576(2)
b [Å]	14.466(1)	13.633(1)	14.481(2)
c [Å]	17.303(2)	36.722(7)	14.528(2)
α [°]	103.81(1)	90	60.62(1)
β [°]	102.14(1)	90	64.63(1)
γ [°]	114.14(1)	120	85.42(1)
V [Å ³]	2749(1)	5911(1)	2054.4(7)
D _c [g cm ⁻³]	2.62	2.01	2.26
Z	4	6	2
μ(Mo-K _α) [cm ⁻¹]	165.4	113.5	110.3
Cryst. dim. [mm]	0.2/0.3/0.5	0.1/0.2/0.45	0.07/0.15/0.55
T [°C]	-68	-68	-68
Abs. correction	empirical	empirical	empirical
T _{min} /T _{max} [%]	44.04/99.82	33.35/99.88	41.54/99.80
scan mode	θ	ω	ω
scan range (θ) [°]	2-27	2-26	2-27
hkl-range	16/±18/±22	-16/16/±45	±16/±18/18
measured data	11936	5480	8896
unique data	9472	2458	8093
observed data	7902	1889	6853
No. of parameters	499	96	473
Obs. criterion	F _o ≥ 4σ(F _o)	F _o ≥ 4σ(F _o)	F _o ≥ 4σ(F _o)
R [*]	0.049	0.049	0.030
R _w **	0.043	0.051	0.025
Weighting scheme	w = {σ ² (F _o) + 0.000276 F _o ² }] ⁻¹	w = {σ ² (F _o) + 0.001207 F _o ² }] ⁻¹	w = {σ ² (F _o) + 0.000059 F _o ² }] ⁻¹
Residual density [e Å ⁻³]	2.96/-1.72	2.84/-1.71	1.21/-1.55

$$* R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ** R_w = \frac{\sum w (|F_o| - |F_c|)^2}{\sum w F_o^2}^{1/2}$$

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