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Acylseleno- and acylthioureato complexes of gold(i) N-heterocyclic carbenes†

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A series of gold(i) N-heterocyclic carbene complexes containing monoanionic acylchalcogenourea (chalcogen = S, Se) ligands was prepared and characterised by various spectroscopic methods and X-ray diffraction. The compounds were conveniently accessible in good yields through a one-pot reaction involving [AuCl(tht)] (tht = tetrahydrothiophene), the imidazolium salt and the acylchalcogenourea in the presence of excess base. The X-ray diffraction experiments showed that in these complexes, the normally chelating ligands adopt the rare κ S/Se-coordination mode in which only the chalcogen is bound to gold.

Introduction

Acylselenoureas are bidentate Se,O-ligands, which, upon deprotonation typically form six-membered chelate rings with a large variety of metals. Examples for such compounds include bis(chelates) with the divalent transition metal ions Cu²⁺, Ni²⁺, Pd²⁺, Pt²⁺, Zn²⁺ and Cd²⁺.^{1–10} There are also examples of tris(chelates) with the trivalent metal ions Fe³⁺, Co³⁺ and In³⁺.^{11–13} Amongst the main group elements, bis(chelates) containing lead(II) have been of recent interest as single-source precursors for various PbSe nanomaterials.^{14,15} However, examples of such species containing silver and gold are still quite rare. We have previously reported the first Ag⁺ and Au⁺ compounds containing acylselenoureato and acylthioureato ligands together with a detailed study of their biological activity.^{16–19} We also demonstrated that square planar gold(III) complexes with acylselenoureato ligands are accessible when a dicarbanionic co-ligand is present.²⁰ This stabilizing co-ligand is essential to prevent reduction of gold by the acylselenourea during the reaction. Given our interest in gold complexes with selenium and sulfur ligands,²¹ we communicate here the synthesis of some gold(i) complexes containing acylselenoureas and acylthioureas with an N-heterocyclic carbene co-ligand by a simple one-pot process.

Results and discussion

Initially, we examined three different routes towards the desired NHC-gold(i) acylchalcogenoureato complexes: (1) the reaction of

the acylchalcogenoureas with [AuCl(IPr)] [IPr = 1,3-di(2,6-diisopropylphenyl)imidazolyliene] in the presence of base, (2) the reaction of the acylchalcogenoureas with [AuOH(IPr)] and (3) by transmetalation of [AuCl(IPr)] with the corresponding silver(i) acylchalcogenoureato complexes.¹⁷ To our surprise, the latter two routes afforded either no products at all or we observed formation of dark, inseparable mixtures. In particular, the lack of reactivity of the gold(i) hydroxy complex [AuOH(IPr)] in this system is somewhat unexpected. The Nolan group has previously demonstrated that this reagent readily reacts with a variety of species containing acidic protons to form the corresponding gold(i) complexes.²² Given that the reaction between the acylchalcogenoureas and [AuCl(IPr)] showed the most promising results, we planned to further simplify and generalise the synthesis route by preparing [AuCl(IPr)] *in situ* directly from the imidazolium salt and [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of base and the acylchalcogenoureas. Gratifyingly, the one-pot reaction of [AuCl(tht)] with the acylchalcogenoureas and the imidazolium salt in the presence of two equivalents of KO^tBu afforded the desired complexes in two hours at room temperature in pure form and good yields (Scheme 1).

Complexes **1–4** were isolated as air-, light- and moisture-stable colourless or yellow compounds in yields greater than 60%. The proton NMR spectra of the compounds lack the signal of the NH-proton, consistent with the presence of the deprotonated acylchalcogenourea ligands. Furthermore, the signal due to the carbenic carbon-atom bound to gold can be observed at around 186 ppm (in selenium compounds **1** and **2**) or 183 ppm (in sulfur compounds **3** and **4**) in their ¹³C NMR spectra. These values are higher than that found in the starting material [AuCl(IPr)] (175 ppm),²³ confirming that substitution of the chlorido ligand has indeed occurred. Similar chemical shifts for the carbene-carbon-atom have been observed in other

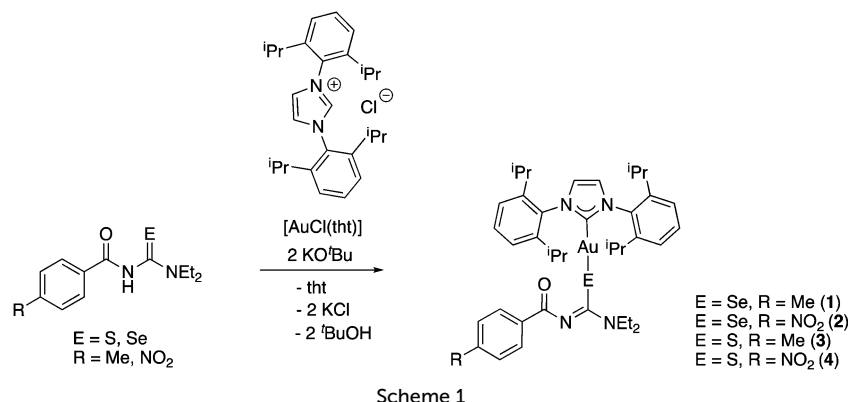
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gold(I) NHC-complexes containing anionic chalcogen ligands.^{24,25} For the selenium compounds we were able to record ⁷⁷Se NMR spectra, which showed singlet resonances shifted upfield by 371 ppm (1) and 380 ppm (2), relative to those of the acylselenoureas themselves.¹⁸ For comparison, the singlet resonances of the triphenylphosphine counterparts of 1 and 2 are shifted upfield by 279 ppm and 266 ppm, respectively.¹⁶ This nicely illustrates the electronic differences that phosphine (Ph₃P) or carbene (IPr) ligands *trans* to the selenium atom have on its ⁷⁷Se chemical shift.

We managed to grow crystals of complexes 1, 2 and 4 suitable for an X-ray diffraction experiment. The compounds crystallise in the monoclinic crystal system in the space groups *P*₂₁/*n*, *P*₂₁/*c* and *C*2/*c*, respectively. The asymmetric unit of 1 contains a single molecule of the complex together with one molecule of co-crystallised ethanol. Compounds 2 and 4 contain four and three independent molecules, respectively in their asymmetric units. The differences in geometric parameters (bond distances and angles) of the independent molecules are however insignificant. In all three complexes the gold atom is bound to the carbon-atom of the IPr-ligand and a selenium or sulfur atom from the deprotonated acylchalcogenourea ligands (Fig. 1–3).

The metal centre is two-coordinate linear with C–Au–Se/S angles ranging from 174° to 177°, as expected for gold(I) compounds. The angles at the chalcogen atoms are around 100°, similar to what is observed in the solid-state structures of gold(I) compounds with anionic Se/S-ligands. Furthermore, the gold–carbon bond distances of approximately 2.0 Å are typical values for gold(I) carbenes. There is only one other example of an NHC–Au(I) complex containing an anionic selenium ligand (SeCN) which has been structurally characterised.²⁶ In this compound the Au–Se bond length of 2.414 Å is slightly longer than those found in complexes 1 and 2 (around 2.39 Å).

Thus, in these compounds the typically bidentate chelating (*via* Se/S and O-atoms) acylchalcogenoureaato ligands behave as simple monodentate Se[−] or S[−] ligands. The ArC(O) units are rotated by almost 90° away from the CSe- and CS-groups which are bound to the gold centre. There is therefore no interaction whatsoever between the oxygen atom of the acylchalcogenoureaato ligand and the metal. We may invoke the Pearson hard/soft principle to account for this observation: the soft nature of the

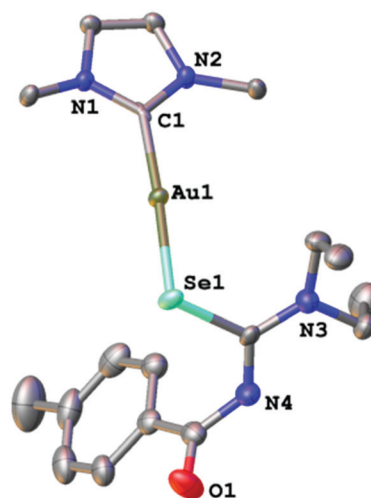


Fig. 1 Molecular structure of 1. Ellipsoids show 30% probability levels. Hydrogen atoms as well as the co-crystallised ethanol of solvation have been omitted for clarity. Only the *ipso* carbon-atoms of the 2,6-ⁱPr₂C₆H₃ groups are shown.

gold(I) centre combined with the soft Se- and S-ligand results in a favourable interaction, whereas the hard-soft mismatch between gold and oxygen disfavors any contact between those atoms. This κSe,S-coordination mode of acylchalcogenoureaato ligands is very rare, apart from our previously reported examples containing gold or rhenium,^{27,40} there are no other examples of structurally characterised metal complexes containing Se-bound monoanionic acylselenourea ligands. In the case of the sulfur counterparts, there are three reports in the literature dealing with κS-coordinated acylthioureaato ligands (Fig. 4).

An early publication from Richter describes the mercury(II) complexes [Hg{PhC(O)NC(S)NR₂}₂] (NR₂ = morpholine, pyrrolidine) featuring κS-bound ligands (Fig. 4 left).²⁸ Although the oxygen atoms are directed towards the metal, the Hg–O distance of 2.52 Å was deemed too large for the S,O-chelating mode. The bis(acylthiourea) derived from isophthaloyl dichloride 1,3-{Et₂NC(S)NHC(O)}₂C₆H₄ reacts with two equivalents of [AuCl(PPh₃)] in the presence of base to afford the corresponding bimetallic gold(I) complex (Fig. 4 centre).²⁹ More recently, Koch reported the platinum(II) complexes [Pt(phen){ArC(O)NC(S)NR₂}₂]



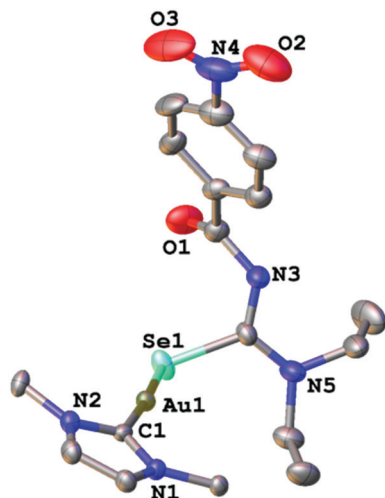


Fig. 2 Molecular structure of one of the independent molecules of **2**. Ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity. Only the *ipso* carbon-atoms of the 2,6- i -Pr₂C₆H₃ groups are shown.

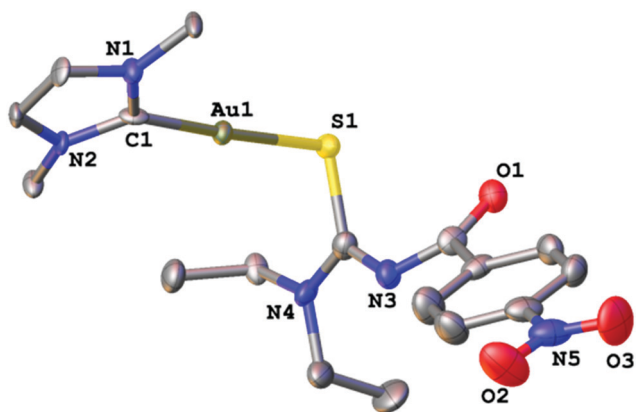


Fig. 3 Molecular structure of one of the independent molecules of **4**. Ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity. Only the *ipso* carbon-atoms of the 2,6- i -Pr₂C₆H₃ groups are shown.

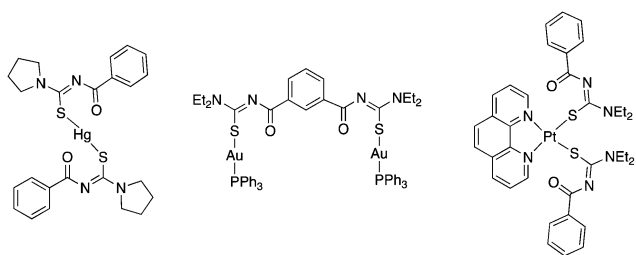


Fig. 4 Known complexes featuring κ S-coordination of acylthiourea ligands.

(Ar = 1-nap, R = n Bu; Ar = Ph, R = Et), in which two deprotonated acylthiourea ligands are κ S-bound to the metal centre (Fig. 4 right).³⁰

In summary we disclose here the first examples of gold(i) carbene complexes containing Se- or S-bound acylchalcogenourea to ligands.

The compounds are readily accessible through a one-pot method starting from readily available materials. We are currently exploring the scope of this method with respect to the carbene co-ligand and potential biological activity of this new class of substances.

Experimental

General

Reactions were carried out under aerobic conditions using HPLC grade solvents. The acylchalcogenourea, ^{31–33} [AuCl(tht)]³⁴ and the imidazolium salt IPrHCl³⁵ were prepared by reported procedures. All other reagents and solvents were procured from commercial suppliers and were used as received. NMR spectra were recorded on Bruker Avance 400 or Bruker Avance III 600 instruments. Spectra were referenced externally to Me₄Si (¹H, ¹³C) and Me₂Se (⁷⁷Se). Elemental analyses were performed by staff of the in-house elemental analysis facility using an Elementar Vario EL system.

Preparation of the complexes

To a solution containing the respective acylchalcogenourea, [AuCl(tht)] (1 equiv.) and IPrHCl (1 equiv.) in MeOH (15 mL) was added KO^tBu (2.2 equiv.). After ca. 2 h at room temperature, the mixture was evaporated to dryness and the residue was extracted into CH₂Cl₂ (3 × 10 mL). The combined extracts were filtered through Celite and the filtrate was subsequently dried in vacuum.

[IPrAu{4-MeC₆H₄C(O)NC(Se)NET₂}] (**1**). This was prepared as described above from 4-MeC₆H₄C(O)NHC(Se)NET₂ (0.038 g, 0.128 mmol), [AuCl(tht)] (0.041 g, 0.128 mmol), IPrHCl (0.054 g, 0.128 mmol) and KO^tBu (0.032 g, 0.282 mmol). A colourless product was isolated in 75% yield (0.085 g). ¹H-NMR (600 MHz, CDCl₃): δ [ppm] = 0.96 (t, J = 6.9 Hz, 6 H, NCH₂CH₃), 1.21 (d, J = 6.9 Hz, 12 H, Me-ⁱPr), 1.25 (d, J = 6.9 Hz, 12 H, Me-ⁱPr), 2.37 (s, 3 H, Me), 2.54 (hept., J = 6.8 Hz, 4 H, CH-ⁱPr), 3.40 (q, J = 7.1 Hz, 4 H, NCH₂CH₃), 7.09 (d, J = 7.9 Hz, 2 H, C₆H₄), 7.15 (s, 2 H, imidazole H), 7.26 (d, J = 7.8 Hz, 4 H, IPr), 7.50 (t, J = 7.8 Hz, 2 H, IPr), 7.81 (d, J = 8.1 Hz, 2 H, C₆H₄). ¹³C-NMR (150 MHz, CDCl₃): δ [ppm] = 13.5 (NCH₂CH₃), 21.5 (Me), 24.0 (Me-ⁱPr), 24.4 (Me-ⁱPr), 28.7 (CH-ⁱPr), 45.1 (NCH₂CH₃), 122.9 (imidazole C), 124.1 (IPr), 128.1 (C₆H₄), 129.8 (IPr), 130.5 (IPr), 134.1 (IPr), 135.2 (C₆H₄), 140.3 (C₆H₄), 145.7 (IPr), 153.2 (CSe), 175.3 (CO), 186.8 (CAu). ⁷⁷Se-NMR (76 MHz, CDCl₃): δ [ppm] = 105.1. Elemental analyses calcd for C₄₀H₅₃N₄OSeAu (881.8): C 54.48, H 6.06, N 6.35; found: C 54.13, H 6.09, N 6.25%. X-ray quality crystals were obtained by vapour diffusion of hexanes into an ethanolic solution of the compound.

[IPrAu{4-O₂NC₆H₄C(O)NC(Se)NET₂}] (**2**). This was prepared as described above from 4-O₂NC₆H₄C(O)NHC(Se)NET₂ (0.041 g, 0.125 mmol), [AuCl(tht)] (0.040 g, 0.125 mmol), IPrHCl (0.053 g, 0.125 mmol) and KO^tBu (0.031 g, 0.275 mmol). A yellow product was isolated in 73% yield (0.083 g). ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 0.98 (m, 6 H, NCH₂CH₃), 1.20 (m, 24 H, Me-ⁱPr), 2.51 (m, 4 H, CH-ⁱPr), 3.46 (q, J = 7.1 Hz, 4 H, IPr), 7.16 (s, 2 H, imidazole H), 7.24 (d, J = 7.8 Hz, 4 H, IPr), 7.48 (t, J = 7.8 Hz, 2 H, IPr), 8.04 (d, J = 8.9 Hz, 2 H, C₆H₄), 8.12 (d, J = 8.9 Hz, 2 H, C₆H₄).



^{13}C -NMR (100 MHz, CDCl_3): δ [ppm] = 13.3 (NCH_2CH_3), 23.9 ($\text{Me}^{\text{I}}\text{Pr}$), 24.3 ($\text{Me}^{\text{II}}\text{Pr}$), 28.7 ($\text{CH}^{\text{I}}\text{Pr}$), 45.4 (NCH_2CH_3), 122.6 (C_6H_4), 123.0 (imidazole C), 124.1 (IPr), 130.2 (C_6H_4), 130.5 (IPr), 134.0 (IPr), 144.4 (C_6H_4), 145.6 (IPr), 148.8 (C_6H_4), 158.8 (CSe), 171.2 (CO), 186.1 (CAu). ^{77}Se -NMR (76 MHz, CDCl_3): δ [ppm] = 122.4. Elemental analyses calcd for $\text{C}_{39}\text{H}_{50}\text{N}_5\text{O}_3\text{SeAu}$ (912.8): C 51.32, H 5.52, N 7.67; found: C 51.28, H 5.44, N 7.52%. X-ray quality crystals were obtained by vapour diffusion of hexanes into a methanolic solution of the compound.

[IPrAu{4-MeC₆H₄C(O)NC(S)NEt₂}] (3). This was prepared as described above from 4-MeC₆H₄C(O)NHC(S)NEt₂ (0.034 g, 0.136 mmol), [AuCl(tht)] (0.044 g, 0.136 mmol), IPrHCl (0.058 g, 0.136 mmol) and KO^tBu (0.034 g, 0.299 mmol). A colourless product was isolated in 61% yield (0.070 g). ^1H -NMR (400 MHz, CDCl_3): δ [ppm] = 0.96 (t, J = 7.1 Hz, 6 H, NCH_2CH_3), 1.19 (d, J = 6.9 Hz, 12 H, $\text{Me}^{\text{I}}\text{Pr}$), 1.21 (d, J = 6.9 Hz, 12 H, $\text{Me}^{\text{II}}\text{Pr}$), 2.37 (s, 3 H, Me), 2.50 (hept., J = 6.9 Hz, 4 H, $\text{CH}^{\text{I}}\text{Pr}$), 3.41 (q, J = 7.1 Hz, 4 H, IPr), 7.07 (d, J = 7.9 Hz, 2 H, C_6H_4), 7.14 (s, 2 H, imidazole H), 7.24 (d, J = 7.8 Hz, 4 H, IPr), 7.48 (t, J = 7.8 Hz, 2 H, IPr), 7.79 (d, J = 8.1 Hz, 2 H, C_6H_4). ^{13}C -NMR (150 MHz, CDCl_3): δ [ppm] = 13.4 (NCH_2CH_3), 21.5 (Me), 23.9 ($\text{Me}^{\text{I}}\text{Pr}$), 24.4 ($\text{Me}^{\text{II}}\text{Pr}$), 28.7 ($\text{CH}^{\text{I}}\text{Pr}$), 44.4 (NCH_2CH_3), 123.0 (imidazole C), 124.1 (IPr), 128.0 (C_6H_4), 129.6 (IPr), 130.5 (IPr), 134.0 (IPr), 135.7 (C_6H_4), 139.9 (C_6H_4), 145.6 (IPr), 163.7 (CS), 174.1 (CO), 184.2 (CAu). Elemental analyses calcd for $\text{C}_{40}\text{H}_{53}\text{N}_4\text{OSAu}$ (834.9): C 57.54, H 6.71, N 6.84; found: C 56.85, H 6.32, N 6.70%.

[IPrAu{4-O₂NC₆H₄C(O)NC(S)NEt₂}] (4). This was prepared as described above from 4-O₂NC₆H₄C(O)NHC(S)NEt₂ (0.030 g, 0.107 mmol), [AuCl(tht)] (0.034 g, 0.107 mmol), IPrHCl (0.046 g, 0.107 mmol) and KO^tBu (0.026 g, 0.235 mmol). A yellow product was isolated in 85% yield (0.079 g). ^1H -NMR (600 MHz, CDCl_3):

δ [ppm] = 1.01 (t, J = 6.9 Hz, 6 H, NCH_2CH_3), 1.16–1.20 (m, 24 H, $\text{Me}^{\text{I}}\text{Pr}$), 2.48 (hept., J = 6.9 Hz, 4 H, $\text{CH}^{\text{I}}\text{Pr}$), 3.48 (q, J = 7.0 Hz, 4 H, IPr), 7.15 (s, 2 H, imidazole H), 7.23 (d, J = 7.8 Hz, 4 H, IPr), 7.46 (t, J = 7.8 Hz, 2 H, IPr), 8.03 (d, J = 8.9 Hz, 2 H, C_6H_4), 8.11 (d, J = 8.9 Hz, 2 H, C_6H_4). ^{13}C -NMR (150 MHz, CDCl_3): δ [ppm] = 13.1 (NCH_2CH_3), 23.8 ($\text{Me}^{\text{I}}\text{Pr}$), 24.3 ($\text{Me}^{\text{II}}\text{Pr}$), 28.6 ($\text{CH}^{\text{I}}\text{Pr}$), 45.1 (NCH_2CH_3), 122.5 (imidazole C), 123.1 (IPr), 124.1 (IPr), 130.1 (IPr), 130.6 (C_6H_4), 133.9 (IPr), 145.0 (IPr), 145.6 (C_6H_4), 148.5 (C_6H_4), 169.3 (CS), 170.9 (CO), 183.4 (CAu). Elemental analyses calcd for $\text{C}_{39}\text{H}_{50}\text{N}_5\text{O}_3\text{SAu}$ (865.9): C 54.10, H 5.82, N 8.09; found: C 53.95, H 5.68, N 7.88%. X-ray quality crystals were obtained by vapour diffusion of hexanes into a methanolic solution of the compound.

X-ray crystallography

Diffraction data for complexes **2** and **4** were collected using an Enraf-Nonius KappaCCD system located in front of a FR591 rotating anode equipped with an Incoatec focusing Montel optic for Mo radiation and an Oxford Cryosystems Cryostream 700. For data integration the EVAL-14 package³⁶ was employed. For data scaling and absorption correction (combination of Gaussian and multiscan corrections) SADABS was used. Diffraction data for complex **1** was collected using a Rigaku Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package.³⁷ All crystal structures were solved using SHELXT³⁸ and refined using SHELXL.³⁸ The Olex2 graphical user interface³⁹ was used for all structure manipulations and for molecular graphics. Crystallographic and refinement details are collected in Table 1.

Table 1 Crystallographic and refinement details for complexes **1**, **2** and **4**

	1 EtOH	2	4
CCDC code	1907692	1907635	1907634
Empirical formula	$\text{C}_{42}\text{H}_{59}\text{AuN}_4\text{O}_2\text{Se}$	$\text{C}_{39}\text{H}_{50}\text{AuN}_5\text{O}_3\text{Se}$	$\text{C}_{39}\text{H}_{50}\text{AuN}_5\text{O}_3\text{S}$
Colour	Colourless	Yellow	Colourless
Formula weight (g mol^{-1})	927.85	912.76	865.86
Temperature (K)	150(2)	100(2)	100(2)
Wavelength (\AA)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
Unit cell dimensions	$a = 14.1899(3) \text{ \AA}$ $b = 16.2803(4) \text{ \AA}$ $c = 18.4131(5) \text{ \AA}$ $\beta = 101.693(2)^\circ$	$a = 19.003(7) \text{ \AA}$ $b = 21.806(3) \text{ \AA}$ $c = 37.911(6) \text{ \AA}$ $\beta = 91.39(2)^\circ$	$a = 33.860(7) \text{ \AA}$ $b = 36.211(7) \text{ \AA}$ $c = 19.899(3) \text{ \AA}$ $\beta = 107.145(18)^\circ$
Volume	$4165.47(18) \text{ \AA}^3$	$15705(7) \text{ \AA}^3$	$23314(8) \text{ \AA}^3$
Z	4	16	24
ρ_{calc}	1.480 g cm^{-3}	1.544 g cm^{-3}	1.480 g cm^{-3}
μ	4.444 mm^{-1}	4.716 mm^{-1}	3.882 mm^{-1}
$F(000)$	1872.0	7296.0	10512
Crystal size	$0.03 \times 0.06 \times 0.12 \text{ mm}$	$0.05 \times 0.12 \times 0.18 \text{ mm}$	$0.04 \times 0.05 \times 0.10 \text{ mm}$
θ range for data collection	4.758 to 59.144°	2.599 to 32.974°	2.646 to 28.300°
Reflections collected	25 188	405 585	133 811
Independent reflections	9924	58 942	28 915
Parameters	464	1805	1350
Goodness-of-fit on F^2	1.100	1.029	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0388$ $wR_2 = 0.0784$	$R_1 = 0.0614$ $wR_2 = 0.1157$	$R_1 = 0.0659$ $wR_2 = 0.1048$
Largest difference peak/hole	$3.06/-1.38 \text{ e \AA}^{-3}$	$6.7/-3.6 \text{ e \AA}^{-3}$	$1.4/-2.0 \text{ e \AA}^{-3}$



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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