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# Synthesis, characterisation and biological activity of cycloaurated organogold(III) complexes with imidate ligands

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**Abstract**

The reactions of the cycloaurated gold(III) complexes (2-bp)$AuCl_2$ (2-bp = 2-benzylpyridyl) or (damp)$AuCl_2$ (damp = $Me_2NCH_2$-$C_6H_4$) with an excess of sodium saccharinate (Nasacc), potassium phthalimidate (Kphth), or with isatin and trimethylamine in refluxing methanol results in the successful isolation of a series of new gold(III) imidate complexes. These were characterised by NMR and IR spectroscopies, and by X-ray structure determinations on (2-bp)Au(sacc)$_2$ and (2-bp)Au(phth)$_2$. In both structures, the planes of the saccharinate and the phthalimidate ligands are orientated almost perpendicular to the gold coordination plane. As expected from *trans*-influence considerations, the Au–$N_{(imidate)}$ bond lengths *trans* to the aryl carbon atoms are longer than the Au–$N_{(imidate)}$ bond lengths *trans* to the pyridyl groups. The complexes have also been characterised by electrospray ionisation MS; in the presence of halide ligands, one imidate ligand is readily displaced. Anti-tumour (P388 murine leukemia) and selected anti-microbial data for the new complexes are reported. Surprisingly, all three damp complexes had low anti-tumour activity, which is likely to be a consequence of the poor solubility of these complexes. The synthesis and characterisation of a related gold(III) bis(amidate) complex derived from sulfathiazole is also described.


*Keywords:* Gold complexes; Imidate ligands; Crystal structures; Electrospray mass spectrometry; Biological activity

## 1. Introduction

The search for potent anti-tumour activity has been one of the driving forces for recent activity in the chemistry of cycloaurated gold(III) complexes [1–3], in light of the well-developed medicinal chemistry of platinum(II), and the similarities between this metal centre and gold(III), imparted by their isoelectronic nature. In cycloaurated complexes, the ligand, typically a bidentate nitrogen–carbon donor, stabilises the square-planar gold(III) state towards reduction. Most work has been carried out with the damp complex **1** [1], because of its typical good solubility characteristics and tendency to promote good anti-tumour activity in the corresponding acetate derivative. Developments in this area have been thoroughly reviewed [4,5].

We have been investigating the synthesis and biological properties of cycloaurated complexes that contain a range of ancillary ligands, derived from both the damp system as well as other cycloaurated complexes that are more readily prepared in one step from $HAuCl_4$. Complexes containing chelating thiosalicylate ($SC_6H_4CO_2$) ligands have been found, by ourselves [6,7] and others [8], to show promising biological activity, and we have recently turned our attention to the investigation of complexes with nitrogen and oxygen donor ligands. Examples of catecholate [9], amidophenolate [9], ureylene [10], lactam [11], and auracyclic bis(amidate) [12] complexes have all been prepared, with a number showing promising anti-tumour activity. In this paper, we report studies on the synthesis, characterisation and biological activity of cycloaurated gold(III) complexes containing monodentate imidate ligands derived from saccharin, phthalimide and isatin.

Although imidate derivatives of cycloaurated complexes are new, gold(III) imidate complexes have a long

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history. As long ago as 1929, Pope filed a patent claiming to have synthesised a range of gold(III) succinimidate complexes [13]. Subsequently, Kharasch and Isbell reported [14] the formation of gold(III) imidate complexes $[Au(imidate)_4]^-$ (imidate = anion of succinimide, phthalimide, saccharin or diethyl barbituric acid), which were reformulated by Tyabji and Gibson [15]. Malik et al. [16] demonstrated that the product of the reaction between $[AuCl_4]^-$ and *N*-methylhydantoin was actually a gold(I) complex, and suggested that Kharasch's original Au(III) tetrasuccinimidate complex was also a gold(I) bis(imidate) complex. Only recently, a stable gold(III) complex **2** was reported [17], containing four deprotonated hydantoin ligands, an arrangement thought to be impossible (on steric grounds) by Tyabji and Gibson. Few other gold(III) imidate complexes have been reported, though there are many examples of both gold(I) [18–23] and platinum(II) [24–29] imidate complexes, derived from a range of ligands such as saccharin, phthalimide, and isatin.

## 2. Results and discussion

### 2.1. Synthesis and characterisation of gold(III) imidate complexes derived from saccharin, phthalimide and isatin

The reactions of (damp)$AuCl_2$ (**1**) or (2-bp)$AuCl_2$ (**3**) with an excess of either sodium saccharinate (Nasacc), potassium phthalimidate (Kphth) or isatin (Hisa) in refluxing methanol afforded products **4**–**9** in good yields. The reactions involving isatin required the use of $Me_3N$ to remove the imide proton whereas preformed salts of saccharin and phthalimide were used, and additional base was unnecessary for these ligands. The products **4**–**9** were characterised by ESI MS, NMR and IR spectroscopies, together with elemental microanalysis. The damp complexes **5** and **9** were, surprisingly, only sparingly soluble in $(CH_3)_2SO$ and $CDCl_3$, but the other complexes were soluble in common organic solvents such as dichloromethane, acetone and $(CH_3)_2SO$.

$^1$H NMR spectroscopy of the 2-benzylpyridyl derivatives was used to determine sample purity, however full assignment proved difficult due to the presence of four non-equivalent aromatic rings and hence the presence of complex multiplets in the aromatic region. The methylene protons of the benzylpyridyl ligand are expected to appear as a doublet of doublets, due to geminal coupling between protons in equatorial and axial environments of a puckered six-membered ring, as previously described by Fuchita et al. [30] In the phthalimide **6** and isatin **8** derivatives, the $CH_2$ signals were very broad and barely visible above the baseline, as illustrated in Fig. 1 for (2-bp)Au(phth)$_2$ (**6**); heating effected convergence of the two broad methylene proton signals, giving a broad singlet (Fig. 1). For the saccharin derivative **4** the $CH_2$ resonances were resolved into two broad doublets.

The $^1$H NMR spectrum of (damp)Au(phth)$_2$ (**7**) showed two singlets at $\delta$ 3.32 and 4.53 due to the methyl and

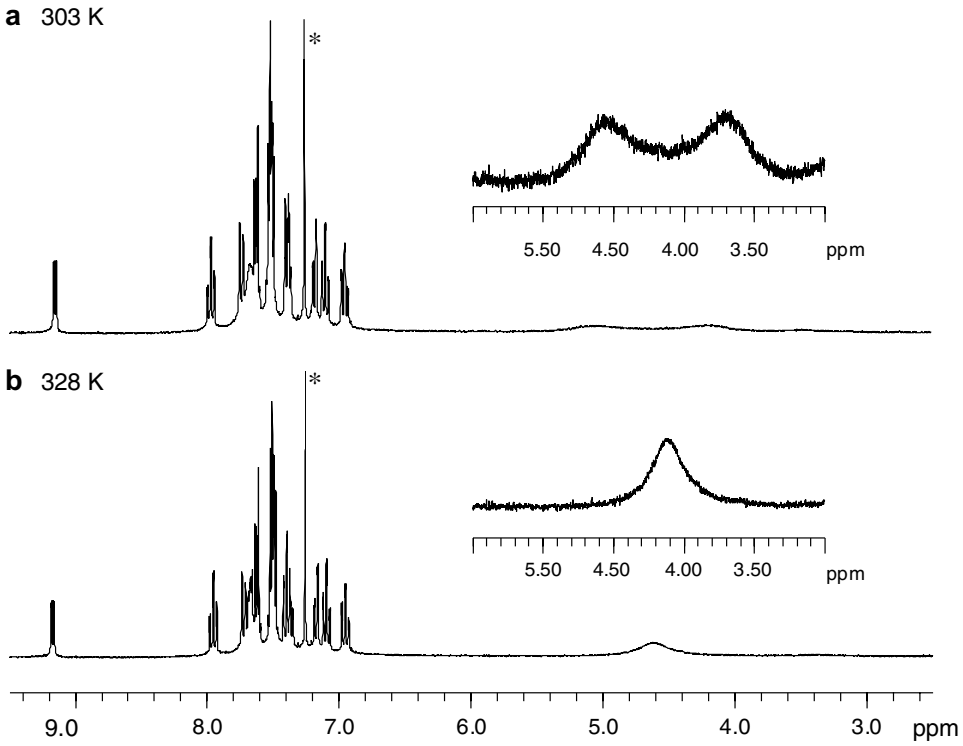



Fig. 1. $^1$H NMR spectra (300 MHz) of the complex (2-bp)Au(phth)$_2$ (**6**) at temperatures of (a) 303 K and (b) 328 K, in $CDCl_3$ solution, showing the fluxionality of the benzylpyridyl group. The peaks marked * are due to $CHCl_3$ (7.26 ppm).

methylene protons of the damp ligand, respectively; this complex contains a plane of symmetry co-planar to the gold coordination plane. However, both (damp)Au(sacc)$_2$ (**5**) and (damp)Au(isa)$_2$ (**9**) were poorly soluble in all common NMR solvents with the exception of $CDCl_3$, in which they were soluble enough to acquire very weak spectra. In contrast to the bis(phthalimidate) species, these complexes do not have a plane of symmetry through the Au plane, due to the unsymmetrical nature of the saccharin and isatin ligands. As a result, the methylene and methyl group protons are in different chemical environments giving rise to two singlets from the methyl protons and two doublets (due to geminal H–H coupling) from the methylene protons.

The IR spectrum of isatin shows strong absorptions in the carbonyl region at 1748, 1728 and 1617 $cm^{-1}$; coordination to gold results in a decrease in the stretching frequency of these bands to 1736, 1692 and 1605 $cm^{-1}$ for the benzylpyridyl derivative **8**, and to 1730, 1701, 1682 and 1603 $cm^{-1}$ for the damp derivative **9**. The NH stretch, present at 3192 $cm^{-1}$ in the free ligand, is absent in the spectra of the gold complexes, indicating coordination through the nitrogen atom. This effect was less pronounced in the saccharin and phthalimide complexes, as the regions of interest contained a large number of strong overlapping bands.

The imidate complexes have also been characterised by ESI MS. As the bis(imidate) complexes **4**–**9** are neutral, NaCl was typically added as an ionisation aid. However, along with the anticipated $[M+Na]^+$ ions, a common ion assigned as $[M\text{-imidate}+Cl+Na]^+$ was visible, even at low cone voltages. This ion could either arise from the mono(imidate) complex (as an impurity in the sample) or displacement of an imidate ligand by chloride during ESI MS analysis. The fragment ion $[M\text{-imidate}]^+$ was also often observed and, in some cases, $[M\text{-imidate} + OMe + Na]^+$. In order to ascertain if the chloride ion was displacing the imidate ligand a small amount of $NaBPh_4$ was added as a (chloride-free) sodium source to complex **6**. The ion $[M\text{-imidate}+Cl+Na]^+$ was no longer detected, suggesting that such species are only formed when chloride ions are present. Addition of small amounts of $Et_4NX$ (X = Cl, Br) to **6** also produced additional ions corresponding to $[M\text{-imidate}+X+Et_4N]^+$, providing further evidence that halide ions can displace the imidate ligand. Table 1 details the range of ions observed when complex **6** was analysed in the presence of various ionisation aids. Addition of pyridine (py) exclusively produced the ion $[M-phth+py]^+$. Together, these ESI MS investigations appear to suggest that one of the monodentate imidate ligands is labile towards displacement by halide and other ligands. This is likely to be the imidate ligand *trans* to the high *trans*-influence aryl carbon; studies of the dissociation of acetate from (damp)Au(OAc)$_2$ have previously shown that one acetate, presumably the one *trans* to the aryl group, was also readily labilised [31]. Labilisation of one amidate donor ligand by halide was previously observed for certain auracyclic bis(amidate) species [7], but in general, auracyclic systems are much more robust towards MS-induced fragmentation, or reaction with halide ligands [6,7,9–11].

Table 1
Ions observed in positive-ion ESI mass spectra for the complex (2-bp)Au(phth)$_2$ (**6**) (=M) at a cone voltage of 20 V

| Ionisation aid | Observed ions (*m*/*z*) |
|---|---|
| NaCl | 680 (100%, $[M+Na]^+$), 565 (78%, $[M-phth+MeO+Na]^+$), 569 (35%, $[M-phth+Cl+Na]^+$), 1337 (28%, $[2M+Na]^+$) |
| Pyridine (py) | 590 (100%, $[M-phth+py]^+$) |
| $NaBPh_4$ | 680 (100%, $[M+Na]^+$), 511 (60%, $[M-phth]^+$) |
| $Et_4NCl$ | 676 (100%, $[M-phth+Cl+Et_4N]^+$), 787 (85%, $[M+Et_4N]^+$), 511 (63%, $[M-phth]^+$) |
| $Et_4NBr$ | 787 (100%, $[M+Et_4N]^+$), 722 (67%, $[M-phth+Br+Et_4N]^+$) |

At a cone voltage of 20 V, the compound (damp)Au(sacc)$_2$ (**4**) showed a strong peak in the ESI mass spectrum at *m*/*z* 465 (100% relative intensity) which was assigned as the cation $[(damp)_2Au]^+$. This ion was not observed at higher cone voltages (>40 V), and had considerably reduced intensity when NaCl was added to promote ionisation of the neutral **4**. The cation $[(damp)_2Au]^+$ was not detected in the $^1H$ NMR spectrum but is visible in the ESI spectrum due to it having a high ionisation efficiency, exacerbated by the low solubility of **4**. The analogous methoxy-substituted cation $[(MeO\text{-}damp)_2Au]^+$ has previously been observed in ESI MS analyses [32].

### 2.2. Synthesis and characterisation of a gold(III) sulfathiazole complex

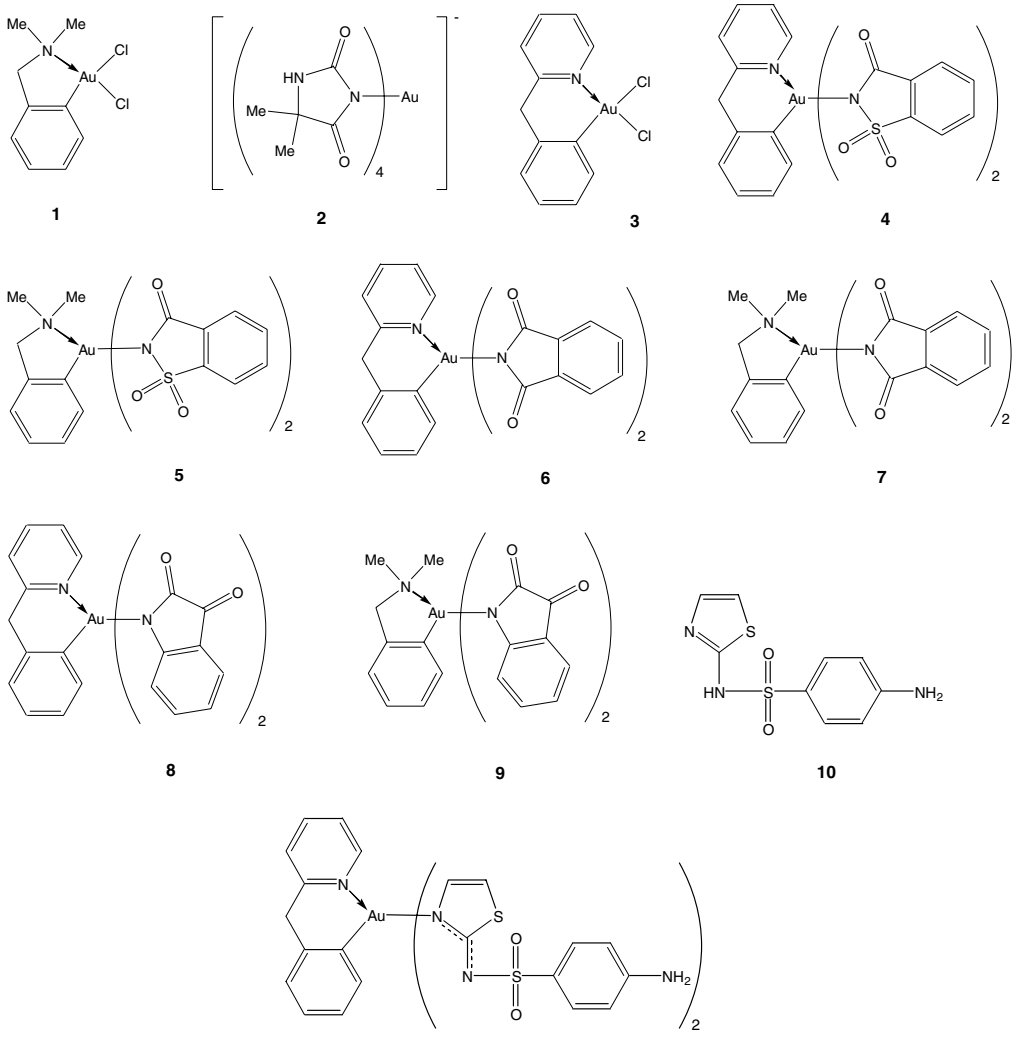
The complex (2-bp)AuCl$_2$ (**3**) was also reacted with sulfathiazole [4-amino-*N*-(thiazol-2-yl)benzenesulfonamide, stzH (**10**)], giving the bis(sulfathiazole) complex **11** in excellent yield as a yellow solid. This complex was poorly soluble in all solvents with the exception of $(CH_3)_2SO$ and $HC(O)NMe_2$ (DMF), but was successfully characterised by NMR, ESI MS, IR, and elemental microanalysis. The mode of co-ordination to the gold is unclear, as sulfathiazole has three available nitrogen binding sites. Attempts at growing X-ray quality single crystals (by slow evaporation of a saturated DMF solution, or by vapour diffusion of methanol into a DMF solution) were unsuccessful thus the structure was unable to be assigned unambiguously. An X-ray crystal structure of the isoelectronic platinum(II) sulfathiazole complex *cis*-[Pt(stz)$_2$(PPh$_3$)$_2$] has confirmed bonding of the sulfathiazole anions through the thiazole nitrogen [33]. Structures of other transition metal [Co(II) [34] and Cu(II) [35]] sulfathiazole complexes indicate the ligand bonded to the metal centre via the thiazole nitrogen. However, an X-ray crystal structure has also been solved showing sulfathiazole bridging two independent Cu atoms through amide and thiazole nitrogens [36].

The $^1$H NMR spectrum of complex **11** was very complicated, however the signal from the amino ($NH_2$) protons was visible, only very slightly shifted ($\delta = 5.69$) from free sulfathiazole ($\delta = 5.75$), indicating that bonding to the gold centre is not through the amino group. The IR spectrum of **11** provides evidence for coordination to the gold through the thiazole nitrogen. Sulfathiazole has a strong absorption at 3350 $cm^{-1}$ due to $NH_2$ stretching and **11** also has absorptions in this region (3430 $cm^{-1}$) suggesting that the $NH_2$ group remains intact. Likewise, the absorptions due to $SO_2$ stretching and bending modes are not greatly shifted upon coordination (1136 and 1323 $cm^{-1}$ in sulfathiazole compared with 1131 and 1323 $cm^{-1}$ in **11**). However, the S–N stretching frequency of the thiazole ring has decreased from 1531 to 1459 $cm^{-1}$ upon coordination, indicating that coordination probably occurs through $N_{thiazole}$. The values obtained are very comparable to the Pt(II) sulfathiazole complexes, again supporting binding through the thiazole nitrogen. This observation has been noted before in other metal-sulfathiazole compounds [37,38].

### 2.3. X-ray crystal structures of (2-bp)Au(sacc)$_2$ (4) and (2-bp)Au(phth)$_2$ (6)

Structure determinations of **4** and **6** were carried out in order to ascertain the geometry and orientation of the saccharinate and phthalimidate ligands around the gold centre. Views of the structures are shown in Figs. 2–5 along with the atom numbering schemes. A comparison of important bond lengths and angles is presented in Table 2, while comparisons of the geometric parameters of the coordinated ligands with free saccharin [39] and phthalimide [40] are given in Tables 3 and 4, respectively.

In both cases, the geometry around the gold atom is essentially square-planar. No atom deviates from the least-squares plane [defined by N(1), N(2), N(3), Au(1) and C(41) for the saccharin derivative **4**; N(1), N(2), N(3), Au(1) and C(12) for the phthalimide derivative **6**] by more than 0.040 or 0.0675 Å, respectively. The Au–$N_{imidate}$ bond lengths in the structures are very comparable; as expected, the Au–$N_{imidate}$ bond lengths *trans* to the benzylpyridyl



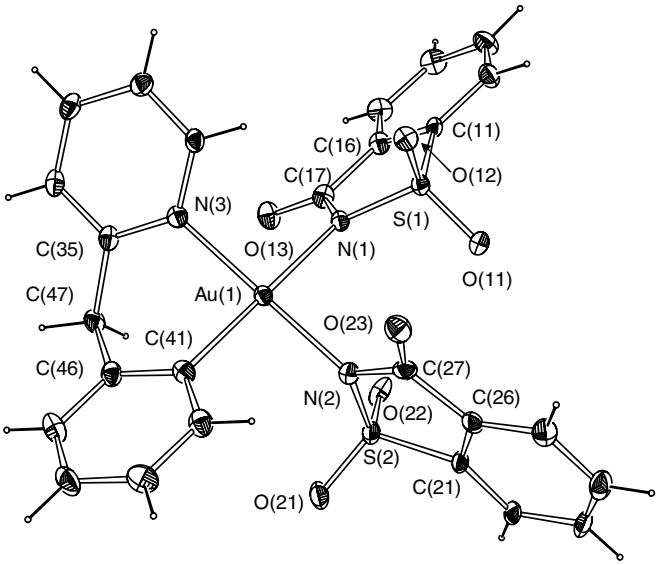



Fig. 2. Perspective view of the X-ray crystal structure of the complex (2-bp)Au(sacc)$_2$ (**4**) showing the atom labelling scheme. Thermal ellipsoids are shown at the 30% probability level. The solvent of crystallisation has been omitted for clarity.

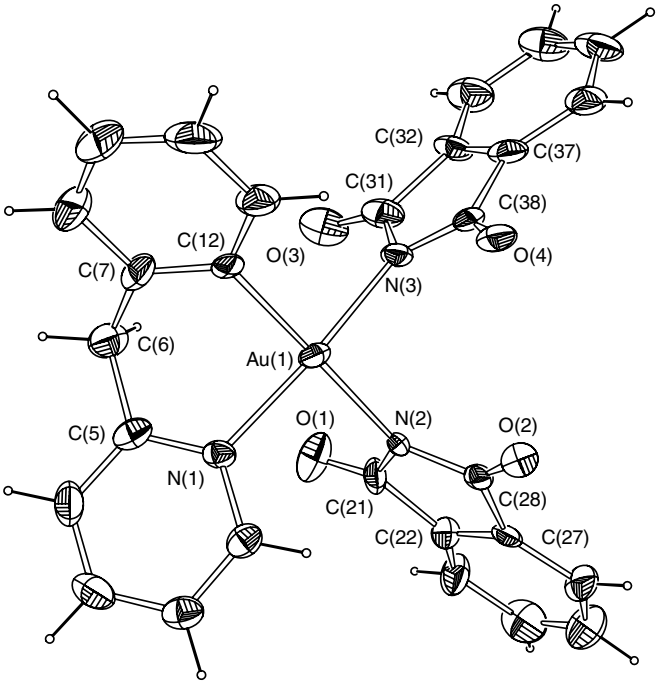



Fig. 3. Perspective view of the X-ray crystal structure of the complex (2-bp)Au(phth)$_2$ (**6**) showing the atom labelling scheme. Thermal ellipsoids are shown at the 50% probability level. The dichloromethane of crystallisation has been omitted.

carbon are longer than those *trans* to the benzylpyridine nitrogen due to the phenyl ligand having a higher *trans* influence than the pyridyl nitrogen ligand [41].

Both saccharinate and phthalimidate ligands are essentially planar. Tables 3 and 4 compare selected bond lengths of the free saccharin and phthalimide molecules with those of the coordinated ligands. Upon coordination to gold, the

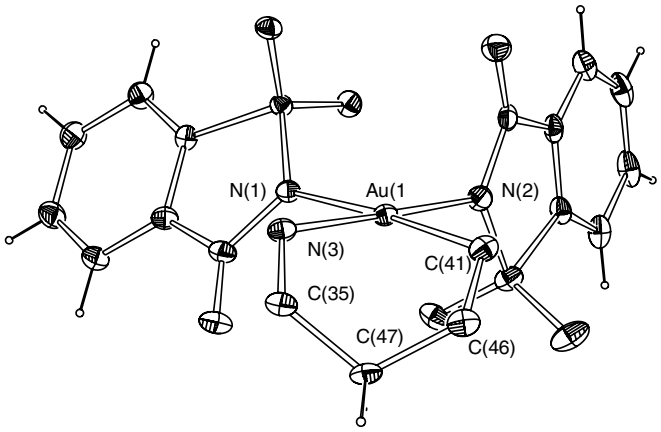



Fig. 4. Side view of the X-ray crystal structure of the complex (2-bp)Au(sacc)$_2$ (**4**) showing the orientation of the saccharinate ligands with respect to the gold coordination plane. Thermal ellipsoids are shown at the 30% probability level. Solvent of crystallisation and the atoms completing the benzyl and pyridyl rings have been omitted for clarity.

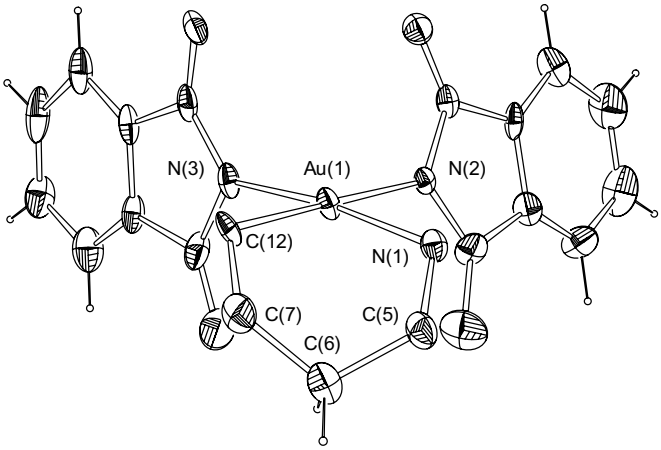



Fig. 5. Side view of the X-ray crystal structure of the complex (2-bp)Au(phth)$_2$ (**6**) showing the orientation of the phthalimidate ligands with respect to the gold coordination plane. Dichloromethane of solvation and atoms completing the benzyl and pyridyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

C=O and S=O bond lengths in the saccharin ligand significantly increase. This effect is less pronounced in the phthalimidate complex.

In both structures, the planes of the saccharin and the phthalimide ligands are orientated almost perpendicular to the coordination plane of the gold (Figs. 4 and 5), most probably to reduce steric interactions between the bulky imidate ligands. This particular ligand orientation has been observed previously in the similar square-planar platinum(II) isatin complex *cis*-[Pt(isat)$_2$(PPh$_3$)$_2$] [42]. In the structure of the saccharin complex **4**, the plane of the ligand coordinated through N(1) has a dihedral angle of 58.70° relative to the gold co-ordination plane, whereas the ligand coordinated through N(2) has an angle of 85.21°. The bis(phthalimide) structure is such that the plane of the phthalimide ligand co-ordinated through

Table 2
Comparison of selected bond lengths (Å) and angles (°) between (2-bp)Au(sacc)$_2$ (**4**) and (2-bp)Au(phth)$_2$ (**6**)

| | **4** | **6** |
|---|---|---|
| *Bonds* | | |
| Au–$N_{benzylpyridyl}$ | 2.041(4) | 2.046(10) |
| Au–$C_{benzylpyridyl}$ | 2.021(4) | 2.041(11) |
| Au–$N_{trans\ to\ C}$ | 2.118(4) | 2.117(9) |
| Au–$N_{cis\ to\ C}$ | 2.015(4) | 2.007(9) |
| *Angles* | | |
| $N_{benzylpyridyl}$–Au–$C_{benzylpyridyl}$ | 89.4(2) | 88.3(4) |
| $N_{cis\ to\ C}$–Au–$N_{trans\ to\ C}$ | 90.4(2) | 90.5(4) |
| $C_{benzylpyridyl}$–Au–$N_{cis\ to\ C}$ | 90.5(2) | 90.2(4) |
| $N_{benzylpyridyl}$–Au–$N_{trans\ to\ C}$ | 89.8(2) | 91.1(4) |

Table 3
Comparison of selected bond lengths (Å) between saccharin and the coordinated saccharinate ligands of **4**

| Bond | Saccharin [28] | Ligand co-ordinated through N(1) | Ligand co-ordinated through N(2) |
|---|---|---|---|
| C=O | 1.214 | 1.221(5) | 1.216(6) |
| S=O | 1.409 | 1.444(3) | 1.434(3) |
| | 1.429 | 1.444(3) | 1.443(3) |
| N–C | 1.369 | 1.389(6) | 1.383(6) |
| N–S | 1.633 | 1.647(4) | 1.662(4) |

Table 4
Comparison of selected bond lengths (Å) between phthalimide and the coordinated phthalimidate ligands of **6**

| Bond | Phthalimide [29] | Ligand co-ordinated through N(2) | Ligand co-ordinated through N(3) |
|---|---|---|---|
| C=O | 1.216 | 1.212(15) | 1.228(17) |
| | 1.222 | 1.237(16) | 1.235(16) |
| C–N | 1.381 | 1.367(14) | 1.363(16) |
| | 1.395 | 1.382(16) | 1.387(17) |

N(2) is at an angle of 71.60°, while the N(3)-coordinated ligand is at an angle of 89.53°, with respect to the gold coordination plane.

Interestingly, the saccharin ligands are orientated so that the $SO_2$ groups are *trans* to each other, as seen in Fig. 4. Although no crystal structures of square-planar bis(saccharin) metal complexes could be found in the literature, the arrangement of the two $SO_2$ groups *trans* to each other appears to be a common trend. Examples of six co-ordinate octahedral structures where the $SO_2$ groups occupy opposite binding sites in a *trans* configuration are vast [43]. In square pyramidal complexes there are examples of both *cis* [44] and *trans* [45] arrangements of the saccharinate ligands. Interestingly, in the linear Hg(saccharinate)$_2$ molecule the saccharinate ligands are orientated so the $SO_2$ groups are positioned on the same side [46].

## 3. Biological activity

The anti-tumour and anti-microbial activities of the bis(imidate) complexes were determined and data are reported in Table 5. The benzylpyridyl complexes **6** and **8** have $IC_{50}$ values that are very comparable to the auracyclic bis(amidate) products reported by us in a previous paper [12]. The other bis(imidate) complexes show low anti-tumour activity towards the P388 murine leukaemia cell line. There are two likely reasons for this. Firstly, the damp complexes **5**, **7** and **9** all have surprisingly low solubilities in common solvents when compared to other damp complexes reported in the literature, where there are many examples often showing excellent anti-tumour activity [1–5]. Secondly, the greater lability of monodentate ligands relative to the more stable and less labile metallacyclic products may have an influence on the biological activity. ESI MS results indicate that one imidate ligand is lost very easily, and such reactions might prevent the complex from reaching its biological target. Continuing the analogy with platinum(II) systems, it is known that replacement of monodentate ligands (such as chloride in cisplatin) with a bidentate chelating ligand (such as cyclobutane-1,1-dicarboxylate in carboplatin) slows the rate of hydrolysis and moderates the toxicity of the platinum-based drug [47].

## 4. Conclusions

New gold(III) bis(imidate) complexes (imidate = anion of saccharin, phthalimide, isatin) have successfully been synthesised and characterised. To the best of our knowledge, these are the first gold compounds of this type to

Table 5
Anti-tumour (P388) and anti-microbial activities for gold(III) bis(imidate) derivatives

| Compound | Anti-tumour $IC_{50}$[a] | | Anti-microbial[b] activity[c] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ng mL$^{-1}$ | μM | Ec | Bs | Pa | Ca | Tm | Cr |
| (2-bp)Au(sacc)$_2$ (**4**) | >25000 | >34.3 | 2 | 7 | 2 | 5 | 2 | – |
| (damp)Au(sacc)$_2$ (**5**) | >25000 | >36.0 | 1 | 4 | – | – | 3 | – |
| (2-bp)Au(phth)$_2$ (**6**) | 3258 | 5.0 | N/T | 10 | N/T | 5 | 5 | N/T |
| (damp)Au(phth)$_2$ (**7**) | >25000 | >40.1 | 2 | 5 | – | 4 | 3 | – |
| (2-bp)Au(isa)$_2$ (**8**) | 6894 | 10.5 | 4 | 8 | 6 | 4 | 5 | – |
| (damp)Au(isa)$_2$ (**9**) | >25000 | >40.1 | 1 | 4 | – | – | 3 | – |

N/T = not tested.

[a] The concentration of the sample required to reduce the cell growth of the P388 leukaemia cell line (ATCC CCL 46) by 50%.

[b] Ec = *Escherichia coli*, Bs = *Bacillus subtilis*, Pa = *Pseudomonas aeruginosa*, Ca = *Candida albicans*, Tm = *Trichophyton mentagrophytes*, Cr = *Cladosporium resinae*.

[c] Inhibition zone as an excess radius (mm) from a 6 mm disc containing 2 μg of sample; – denotes no observed activity.

be reported. The X-ray crystal structures of (2-bp)Au(sacc)$_2$ (**4**) and (2-bp)Au(phth)$_2$ (**6**) have been solved and indicate that the imidate anions are co-ordinated to the gold centre through Au–N bonds. In both cases, the planar imidate ligands are orientated perpendicular to the gold co-ordination plane.

## 5. Experimental

### 5.1. General

General experimental techniques were as previously described [9]; routine ESI mass spectra were recorded on a VG Platform II instrument, using methanol as the mobile phase. Assignment of mass spectrometric isotope patterns was aided by the ISOTOPE program [48]. All NMR spectra were acquired in $CDCl_3$, with the exception of **11** [$(CD_3)_2SO$]. Integration of the $^1$H NMR spectra indicated that **7** and **8** crystallised with approximately 1.0 and 0.12 mol of dichloromethane, respectively.

All reactions were carried out with no attempts to exclude light or air. The solvents used were LR grade. Trimethylamine (Eastman, 25% aqueous solution), sodium saccharinate (Aldrich), potassium phthalimidate (Merck), isatin (BDH) and sulfathiazole (BDH) were used as supplied. The cycloaurated gold(III) complexes (2-bp)$AuCl_2$ (**3**) [49] and (damp)$AuCl_2$ (**1**) [50,51] were prepared by modified literature methods.

### 5.2. Synthesis of (2-bp)Au(sacc)$_2$ (4)

The complex (2-bp)$AuCl_2$ (**3**) (100 mg, 0.23 mmol) and sodium saccharinate (190 mg, 93 mmol) were added to methanol (25 mL) and refluxed with stirring for 2 h. After cooling to room temperature, water (50 mL) was added, resulting in the rapid deposition of white microcrystals. These were filtered, washed with water (2 × 10 mL) and diethyl ether (10 mL) and dried under vacuum to give 158 mg (93%) of product. For microanalysis the crude product was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution of the product at room temperature to give white crystals. M.p. 131–134 °C. *Anal.* Calc. for $C_{26}H_{18}N_3O_6S_2Au$: C, 42.8; H, 2.5; N, 5.8. Found: C, 42.2; H, 2.8; N, 5.5%. IR: $\upsilon$(C=O) 1686 cm$^{-1}$ (s); $\upsilon(SO_2$, sym) 1291 cm$^{-1}$ (s), $\upsilon(SO_2$, asym) 1155 cm$^{-1}$ (br s). ESI MS: Cone voltage 20 V: NaCl added, *m*/*z* 605 (100%, [M-sac+Cl+Na]$^+$). $^1$H NMR, $\delta$ 4.17 (d, 1H), 5.11 (d, 1H), 7.01–8.04 (m, 15H), 9.26 (d, 1H). $^{13}$C–{$^1$H} NMR, $\delta$ 47.5 ($CH_2$), 120.5–157.3 (aryl C), 182.7, 184.5 (*C*=O).

### 5.3. Synthesis of (damp)Au(sacc)$_2$ (5)

The complex (damp)$AuCl_2$ (**1**) (100 mg, 0.25 mmol) and sodium saccharinate (206 mg, 1 mmol) were dissolved in refluxing methanol (30 mL) to give a colourless solution. During two hours of refluxing with stirring, white microcrystals were deposited. These were filtered, washed with water (2 × 10 mL) and diethyl ether (10 mL) then dried under vacuum to give 142 mg (84%) of product. M.p. 196–198 °C (decomp.). *Anal.* Calc. for $C_{23}H_{20}N_3O_6S_2Au$: C, 39.7; H, 2.9; N, 6.0. Found: C, 39.7; H, 3.1; N, 5.9%. IR: $\upsilon$(C=O) 1695 cm$^{-1}$; $\upsilon(SO_2$, sym) 1317, 1291 cm$^{-1}$; $\upsilon(SO_2$, asym) 1159, 1167 cm$^{-1}$. ESMS: Cone voltage 20 V: NaCl added, *m*/*z* 571 (100%, [M-sac+Cl+Na]$^+$), 465 (30%, [(damp)$_2$Au]$^+$), 718 (10%, [M+Na]$^+$); pyridine added, *m*/*z* 592 (100%, [M-sac+py]$^+$). $^1$H NMR, $\delta$ 3.43 (s, 3H), 3.49 (s, 3H), 4.20 (br d, 1H), 5.06 (br d, 1H), 7.09 (t, 1H), 7.13–7.24 (m, 4H), 7.68–7.71 (m, 6H), 8.0 (d, 1H). The compound was too insoluble for a satisfactory $^{13}$C–{$^1$H} NMR spectrum.

### 5.4. Synthesis of (2-bp)Au(phth)$_2$ (6)

The complex (2-bp)$AuCl_2$ (**3**) (200 mg, 0.46 mmol) and potassium phthalimidate (340 mg, 1.8 mmol) were added to methanol (50 mL) and refluxed with stirring for 1 h, during which time a pale yellow solution formed. Water (30 mL) was added, resulting in the immediate deposition of white microcrystals. After cooling to room temperature, the suspension was filtered, washed with water (2 × 10 mL) and diethyl ether (10 mL) then dried under vacuum to give 254 mg (84%) of product. *Anal.* Calc. for $C_{28}H_{18}N_3O_4Au$: C, 51.2; H, 2.8; N, 6.4. Found: C, 50.4; H, 2.8; N, 6.4%. IR: $\upsilon$(C=O) 1690 cm$^{-1}$ (s) and 1664 cm$^{-1}$ (s). ESI MS: Cone voltage 20 V, NaCl added: *m*/*z* 680 (100%, [M+Na]$^+$), 565 (78%, [M−phth+MeO+Na]$^+$), 569 (35%, [M−phth+Cl+Na]$^+$), 1337 (27%, [2M+Na]$^+$). $^1$H NMR, $\delta$ 4.15 (br d, 1H), 5.15 (br d, 1H), 6.95 (t, 1H), 7.10 (t, 1H), 7.17 (d, 1H), 7.38 (m, 3H), 7.51 (m, 5H), 7.62 (m, 2H), 7.69 (d, 1H), 7.97 (t, 1H), 9.15 (d, 1H). $^{13}$C–{$^1$H} NMR, $\delta$ 47.6 ($CH_2$), 122.1–157.8 (aryl *C*), 177.3, 172.8 (*C*=O).

### 5.5. Synthesis of (damp)Au(phth)$_2$ (7)

The complex (damp)$AuCl_2$ (**1**) (100 mg, 0.25 mmol) and potassium phthalimidate (186 mg, 1 mmol) were added to methanol (30 mL) and refluxed with stirring for 2 h, during which time white microcrystals were deposited. The mixture was cooled, filtered then washed with methanol (2 × 10 mL) and diethyl ether (10 mL). The crude product was recrystallised by vapour diffusion of pentane into a dichloromethane solution of the crude product. The colourless crystals were filtered, washed (petroleum spirits) then dried under vacuum to give 133 mg (86%) of product. M.p. 192 °C (decomp.). *Anal.* Calc. for $C_{25}H_{20}N_3O_4Au \cdot 1.06CH_2Cl_2$: C, 43.9; H, 3.1; N, 5.9. Found: C, 44.3; H, 3.1; N, 6.1%. IR: $\upsilon$(C=O) 1686 cm$^{-1}$ (s) and 1655 cm$^{-1}$ (s). ESI MS: Cone voltage 20 V: *m*/*z* 646 (100%, [M+Na]$^+$), 477 (82%, [M−phth]$^+$), 1269 (27%, [2M+Na]$^+$). $^1$H NMR, $\delta$ 3.32 (s, 6H), 4.53 (s, 2H), 5.30 (s, 2.11H, from $CH_2Cl_2$), 6.69 (d, 1H), 7.01 (t, 1H), 7.19, (d, 1H), 7.25 (t, 1H), 7.56 (m, 4H), 7.68 (m, 4H).

$^{13}C$–{$^{1}H$} NMR, $\delta$ 53.5 ($CH_2Cl_2$), 53.0 ($CH_3$), 75.5 ($CH_2$), 122.4–144.5 (aryl *C*), 172.7, 177.5 (*C*=O).

### 5.6. Synthesis of (2-bp)Au(isa)$_2$ (**8**)

The complex (2-bp)$AuCl_2$ (**3**) (200 mg, 0.46 mmol) and isatin (270 mg, 1.84 mmol) were added to refluxing methanol (40 mL). While stirring, trimethylamine (2 mL, excess) was added, resulting in the solution changing from deep red to bright orange. The solution was further refluxed with stirring for 20 min. Water (50 mL) was added, resulting in the deposition of orange microcrystals which were collected by filtration. The crude product was recrystallised from dichloromethane and pentane, filtered, washed with water (2 × 10 mL) and diethyl ether (10 mL) and dried under vacuum to give 266 mg (88%) of **8**. M.p. 225 °C (decomp.). *Anal.* Calc. for $C_{28}H_{18}N_3O_4Au \cdot 0.12CH_2Cl_2$: C, 50.6; H, 2.8; N, 6.3. Found: C, 49.7; H, 3.0; N, 6.3%. IR: $\upsilon$(C=O) 1736 cm$^{-1}$ (s), 1692 cm$^{-1}$ (s) and 1605 cm$^{-1}$ (s). ESI MS: Cone voltage 20 V: *m*/*z* 680 (100%, $[M+Na]^+$), 569 (67%, [M-isa + Cl + Na]), 565 (56%, $[M\text{-isa}+MeO+Na]^+$). $^{1}H$ NMR, $\delta$ 4.35 (br. s, 2H), 5.33 (s, 0.24H, from $CH_2Cl_2$), 6.87 (t, 1H), 6.95 (t, 1H), 7.01 (d, 1H), 7.18–7.51 (m, 11H), 7.81 (d, 1H), 8.06 (t, 1H). $^{13}C$–{$^{1}H$} NMR, $\delta$ 47.7 ($CH_2$), 53.5 ($CH_2Cl_2$), 112.4–157.3 (aryl *C*), 162.9, 166.8, 185.1, 189.0 (*C*=O).

### 5.7. Synthesis of (damp)Au(isa)$_2$ (**9**)

The complex (damp)$AuCl_2$ (**1**) (100 mg, 0.25 mmol) and isatin (148 mg, 1 mmol) were stirred in refluxing methanol (30 mL). Trimethylamine (2 mL, excess) was added, resulting in the solution turning from orange to deep red, and the mixture was refluxed for a further 10 min during which time orange microcrystals were deposited. After cooling to room temperature, the product was filtered, washed with water (2 × 10 mL) and diethyl ether (10 mL) and dried under vacuum to give 117 mg (75%) of product. M.p. 210–212 °C (decomp.). *Anal.* Calc. for $C_{25}H_{20}N_3O_4Au$: C, 48.2; H, 3.2; N, 6.7. Found: C, 47.7; H, 3.4; N, 6.7%. IR: $\upsilon$(C=O) 1730 cm$^{-1}$ (s), 1701 cm$^{-1}$ (m), 1682 cm$^{-1}$ (s), 1603 cm$^{-1}$ (s). ESI MS: Cone voltage 20 V: *m*/*z* 646 (100%, $[M+Na]^+$), 465 (55%, $[(damp)_2Au]^+$), 678 (35%, $[M+Na+MeOH]^+$), 1269 (27%, $[2M+Na]^+$). $^{1}H$ NMR, $\delta$ 3.24 (s, 3H), 3.48 (s, 3H), 4.17 (d, 1H), 4.89 (d, 1H), 6.85 (t, 1H), 6.92 (t, 1H), 7.06–7.39 (m, 13H), 7.43 (t, 1H). The compound was too insoluble for a satisfactory $^{13}C$–{$^{1}H$} NMR spectrum.

### 5.8. Synthesis of (2-bp)Au(stz)$_2$ (**11**)

The complex (2-bp)$AuCl_2$ (**3**) (200 mg, 46 mmol) and sulfathiazole (**10**) (257 mg, 1 mmol) were stirred in refluxing methanol (25 mL). Trimethylamine (2 mL, excess) was added, resulting in the rapid deposition of pale yellow microcrystals. The mixture was refluxed with stirring for a further 2 h before being cooled in ice and filtered. The product was then washed with ice-cold methanol (2 × 10 mL) and diethyl ether (10 mL) before being dried under vacuum giving 324 mg (81%) of **11**. M.p. 194–196 °C (decomp.). *Anal.* Calc. for $C_{30}H_{26}N_7O_4S_4Au$: C, 41.2; H, 3.0; N, 11.2. Found: C, 40.8; H, 3.0; N, 10.9%. IR: $\upsilon$(NH) 3430 cm$^{-1}$ (w), $\upsilon$(SN) 1459 cm$^{-1}$ (vs), $\upsilon$($SO_2$, sym) 1323 cm$^{-1}$ (s), $\upsilon$($SO_2$, asym) 1131 cm$^{-1}$ (s). ESI MS: Cone voltage 20 V: NaCl added, *m*/*z* 677 (100%, $[M\text{-stz}+Cl+Na]^+$), 896 (72%, $[M+Na]^+$). $^{1}H$ NMR, $\delta$ 4.64 (br s, 2H), 5.69 (s, 4H, $NH_2$), 5.75 (br s, 2H), 6.51 (d, 2H), 6.56 (d, 1H), 6.66 (d, 1H), 6.77 (d, 1H), 6.90 (t, 1H), 7.13 (d, 1H), 7.21 (t, 1H), 7.31 (d, 1H), 7.36 (d, 1H), 7.52 (t, 1H), 8.02 (d, 1H), 8.22 (t, 1H), 8.55 (d, 1H). The compound was too insoluble for a satisfactory $^{13}C$–{$^{1}H$} NMR spectrum.

## 6. X-ray crystallography

X-ray intensity data were collected on a Bruker CCD diffractometer using standard procedures and software. Empirical absorption corrections were applied (SADABS) [52]. Structures were solved by direct methods and developed and refined on $F_o^2$ using the SHELX programmes [53] operating under WinGX [54,55]. Hydrogen atoms were included in calculated positions. For both structures there was potential pseudo symmetry which could have led to disorder between the phenyl and pyridyl rings of the cyclometallated ligand. However, as found for other examples [12], the assignment of the metallated C and N atoms could be done unambiguously, showing there was no disorder. As discussed earlier [12]: (i) the N position was revealed with higher electron density than the C in the difference map; (ii) the $U_{iso}$ values for the atoms were similar when refined as allocated, but were quite different if the assignment was reversed, and $R_1$ values increased in each case on changing the assignment; (iii) the differences in the Au–N distances to the sacc or phth ligands were consistent with the expected *trans* influences of C and N as assigned.

### 6.1. Structure of (2-bp)Au(sacc)$_2$ (**4**)

White prism crystals of **4** (M.p. 131–134 °C) were obtained from $CH_2Cl_2$/$Et_2O$.

*Crystal data*: $C_{26}H_{18}AuN_3O_6S_2 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$, $M = 809.04$, orthorhombic, space group *Pccn*, $a = 15.7051(2)$, $b = 18.7045(3)$, $c = 19.5764(1)$ Å, $V = 5750.7(1)$ Å$^3$, $T = 84(2)$ K, $Z = 8$, $D_{calc} = 1.869$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 5.405 mm$^{-1}$, $F(000) = 3168$; 32 131 reflections collected with $2° < \theta < 26°$, 5862 unique ($R_{int} = 0.0309$) used after correction for absorption ($T_{max,min} = 0.521$, 0.385). Crystal dimensions = 0.22 × 0.20 × 0.14 mm$^3$.

When the main molecule had been refined, there was significant residual electron density around special positions with 2-fold symmetry at $\frac{1}{4}, \frac{1}{4}, z$. These appeared to be a mixture of $CH_2Cl_2$ and $Et_2O$, but were very disordered and could not be sensibly modelled. This electron density was

excluded using the SQUEEZE procedure of PLATON [56] and refinement was continued against the modified *hkl* data with just the main molecule.

Refinement on $F_o^2$ converged at $R_1 = 0.0327$ [$I > 2\sigma(I)$] and $wR_2 = 0.0569$ (all data), GoF = 1.140. The structure of **4** is illustrated in Fig. 2, with selected bond parameters summarised in Tables 2 and 3.

### 6.2. Structure of (2-bp)Au(phth)$_2$ (6)

White plate-like crystals of **6** were obtained from $CH_2Cl_2$/pentane at 4 °C.

*Crystal data*: $C_{28}H_{18}AuN_3O_4 \cdot CH_2Cl_2$, $M = 742.35$, monoclinic, space group $P2_1/c$, $a = 12.1739(11)$, $b = 11.9101(9)$, $c = 21.597(2)$ Å, $\beta = 104.58(3)°$, $V = 3030.4(5)$ Å$^3$, $T = 84(2)$ K, $Z = 4$, $D_{calc} = 1.627$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 5.06 mm$^{-1}$, $F(000) = 1440$; 32 727 reflections collected with $2° < \theta < 26°$, 6333 unique ($R_{int} = 0.0779$) used after correction for absorption ($T_{max,min} = 0.687, 0.230$). Crystal dimensions $0.41 \times 0.20 \times 0.08$ mm$^3$.

Residual electron density once the main molecule had been refined appeared to come from $CH_2Cl_2$ in the lattice. Although these features were not very well defined, they could be reasonably successfully modelled as two half-solvent molecules over two sites.

Refinement on $F_o^2$ converged at $R_1 = 0.0717$ [$I > 2\sigma(I)$] and $wR_2 = 0.1942$ (all data), GoF = 1.219. The structure of **6** is illustrated in Fig. 3, with selected bond parameters summarised in Tables 2 and 4.

## 7. Biological assays

Details of the biological assays have been published previously [9].

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## Appendix A. Supplementary data

CCDC 610499 and 610498 contain the supplementary crystallographic data for (**4**) and (**6**). These data can be obtained free of charge via www:http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.08.009.

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