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Journal of Organometallic Chemistry 631 (2001) 41–46

Journal of Organometallic Chemistry

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# Gold(III) thiosalicylate complexes containing cycloaurated 2-arylpyridine, 2-anilinopyridine and 2-benzylpyridine ligands

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Received 12 February 2001; accepted 9 May 2001

**Abstract**

Reactions of the gold(III) dichloride complexes [(N_C)$AuCl_2$] ((N_C) = cycloaurated 2-phenylpyridine, 2-(*p*-tolyl)pyridine, 2-anilinopyridine or 2-benzylpyridine) with thiosalicylic acid (2-mercaptobenzoic acid, $HSC_6H_4CO_2H$) and base gives a series of gold(III) thiosalicylate complexes [(N_C)$Au(SC_6H_4CO_2)$]. A crystal structure determination on the 2-*p*-tolylpyridine derivative is reported, confirming the presence of a chelating thiosalicylate ligand, with the tolyl and thiolate groups mutually *cis*, together with a highly puckered gold–thiosalicylate moiety, and a twisted carboxylate group. The activity of the thiosalicylate complexes against P388 leukaemia cells has been determined. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Gold; Thiosalicylate; Cyclometallated ligands; Biological activity; Crystal structure

## 1. Introduction

As part of our studies into the metallacyclic chemistry of gold(III) complexes, we recently reported the synthesis of several gold(III) complexes (**1**) containing chelated thiosalicylate dianion ligands, which showed high (**1a**) to very high (**1b**) antitumour activity against P388 leukaemia cells [1]. Some platinum(II) thiosalicylate complexes have also shown high antimicrobial and antitumour activity [2]. Gold(III) is isoelectronic with platinum(II), both being $d^8$ with square-planar geometries, and while there have been a very large number of studies on the biological activity of platinum(II) complexes [3], studies on the biological chemistry of gold(III) systems are substantially fewer in number. However, gold(III) complexes have been implicated in the metabolism of gold(I) drugs widely used in the treatment of arthritis [4]. Our interest in the biological properties of thiosalicylate complexes is based on the observation that other gold(III) complexes containing cyclometallated ligands have also shown promising antitumour activity [5], such as the diacetate complex **2** [6], and the dichloride **3a** [7], suggesting that this class of complex offers much potential for the development of novel anti-tumour active compounds. Given our promising initial results with gold(III) thiosalicylate complexes, we are investigating related systems, with the hope of finding improved biological activity.

The synthesis of the dichloride complexes (**3**), used in our previous syntheses of thiosalicylate complexes, requires the use of a several-step synthesis from $H[AuCl_4]$, involving the transmetallation reaction of organomercury complexes [8,9]. In this work we wished to employ more readily-prepared gold(III) dihalide starting complexes, and in recent years, a wide range of gold(III) complexes containing cyclometallated ligands, together with two *cis*-halides (as leaving groups) have been synthesised [10]. Here we have used gold(III) dichloride complexes containing cycloaurated 2-phenylpyridine (**4a**) [11], 2-(*p*-tolyl)pyridine (**4b**), 2-anilinopyridine (**5**) [12,13], and 2-benzylpyridine (**6**) [14] as starting materials for the synthesis of new gold(III) thiosalicylate complexes.

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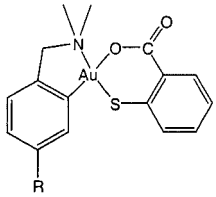
PII: S0022-328X(01)00987-1



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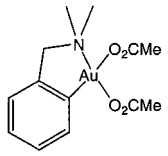

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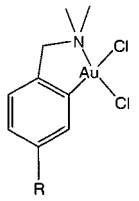

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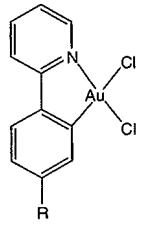

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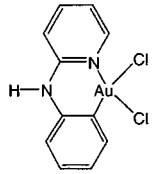

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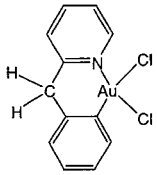

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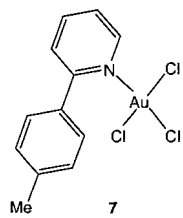
## 2. Results and discussion

### 2.1. Synthesis and characterisation of the gold(III) chloride precursor complex 7

Following the method reported previously for the cycloauration of 2-phenylpyridine [11], the reaction of 2-(*p*-tolyl)pyridine with tetrachloroauric acid in acetonitrile–water solution gives the new gold(III) trichloride complex **7** as bright yellow crystals in 73% yield. Refluxing complex **7** in aqueous acetonitrile for 6 h gave the cycloaurated product **4b** as a pale yellow solid in 38% yield. A longer reaction time was found to be necessary than that reported for the cycloauration of 2-phenylpyridine. Different ratios of MeCN to $H_2O$ in the reaction solvent used did not significantly affect the overall yield of product, and the use of a higher boiling point solvent (propionitrile) led to some decomposition to metallic gold.

Electrospray (ES) mass spectral analysis of **4b** gave ions $[M - Cl + NH_3]^+$ and $[M - Cl + MeCN]^+$ formed by loss of a chloride anion; such ionisation is typical of metal halide complexes [15], and the spectrum was simplified on addition of pyridine, forming the $[M - Cl + \text{pyridine}]^+$ ion.

The *p*-tolyl derivative **4b**, which has not been reported previously, is a potentially very useful starting complex in the study of cyclometallated gold(III) complexes, because the methyl group unambiguously differentiates the phenyl and pyridyl rings, e.g. in X-ray crystal structure determinations. In this regard we also note that Parish and co-workers have recently prepared a range of cycloaurated phenylpyridine derivatives including **4a** and other complexes containing substituents on the pyridine ring, using transmetallation with organomercury derivatives [16].



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### 2.2. Synthesis and characterisation of thiosalicylate complexes

The dihalide complexes **4b**, **5** and **6** react with thiosalicylic acid to give the thiosalicylate complexes **8b**, **9** and **10**, respectively. The simplest method is a one-pot reaction, in methanol solvent using excess triethylamine base; the products are only slightly soluble, and precipitation (and removal of byproduct $Et_3NH^+Cl^-$) is conveniently achieved by addition of water. Alternatively, removal of the chloride ligands of the phenylpyridine complex **4a** with $AgNO_3$, followed by reaction with thiosalicylic acid and NaOH gives the analogue **8a**. The bright yellow, air-stable complexes **8** and **9** are slightly soluble in dichloromethane, while **10** is more soluble. All thiosalicylate complexes give intense $[M + H]^+$ ions in their positive-ion ES spectra, even up to very high cone voltages (for **8b**, up to the maximum for the instrument used, 200 V). The stability of gold(III) complexes containing two chelate rings has been noted previously [1,17]. It is noteworthy that the $[M + Na]^+$, $[2M + Na]^+$ and $[3M + Na]^+$ adduct ions for the ben-

zylpyridine complex **10** were much more intense than for the other complexes.

As with the previous thiosalicylate complexes (**1**), unambiguous determination of which isomer had formed was not possible by NMR spectroscopy (due to the absence of suitable nOe interactions), although the isomer with mutually *cis* C and S donor ligand atoms would be expected, based on antisymbiosis. This has been well documented [18] and is commonly observed in other gold(III) complexes [1,6,19] including ones with sulphur ligands [6,16,20]. The previous structural study on the gold(III)–thiosalicylate complex **1b** was of relatively low quality [1]. Therefore, a single-crystal X-ray diffraction study was carried out on the tolylpyridine complex **8b**.

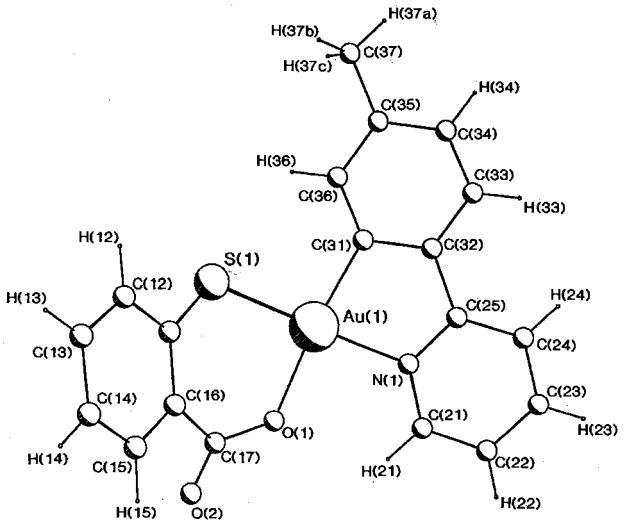



Fig. 1. Molecular structure of complex **8b**, showing the atom numbering scheme.

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **8b**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Au(1)–C(31) | 2.010(3) | Au(1)–N(1) | 2.068(3) |
| Au(1)–O(1) | 2.076(2) | Au(1)–S(1) | 2.2776(8) |
| S(1)–C(11) | 1.776(3) | O(1)–C(17) | 1.309(4) |
| O(2)–C(17) | 1.221(4) | S···O(1) | 3.077(3) |
| *Bond angles* | | | |
| C(31)–Au(1)–N(1) | 81.40(13) | N(1)–Au(1)–O(1) | 92.07(11) |
| C(31)–Au(1)–S(1) | 96.74(10) | O(1)–Au(1)–S(1) | 89.82(8) |
| C(11)–S(1)–Au(1) | 98.59(11) | C(17)–O(1)–Au(1) | 127.6(2) |
| O(2)–C(17)–O(1) | 121.6(3) | O(2)–C(17)–C(16) | 119.7(3) |
| O(1)–C(17)–C(16) | 118.7(3) | | |

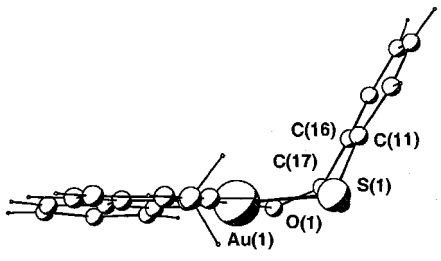
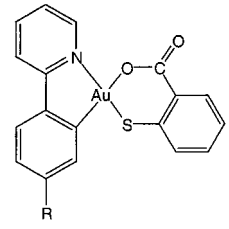



Fig. 2. Side view of complex **8b** showing the puckering of the gold–thiosalicylate system.

The molecular structure of **8b** together with the atom numbering scheme are shown in Fig. 1, while Table 1 gives selected bond lengths and angles. The structure confirms the expected isomer is formed, with the two highest *trans*-influence ligands (aryl carbon and thiolate sulphur) mutually *cis*. The most notable feature regarding the structure is the high degree of non-planarity in the gold thiosalicylate system (Fig. 2). The dihedral angle between the plane of the thiosalicylate ligand (excluding the oxygen atoms) and the Au(III) coordination plane is 59.6 °, much larger than the angles of 30.1 and 37.8 ° found for the two independent molecules of **1b** [1]. This value is however well within the extensive range of 12.4–70.9 ° known for the equivalent fold angles found for Pt(II) thiosalicylate structures [2]. As with the platinum examples, this folding is accommodated by a twist of the carboxylate group from the plane of the rest of the ligand, by 44.1 ° for **8b** which is the largest yet found for any of the gold or platinum examples, the previous record being 38.4 ° for $(Ph_3P)(XyNC)Pt(SC_6H_4CO_2)$ (Xy = 2,6-xylyl) [2].

The Au–S distance in **8b** is 2.277 Å, towards the short end of the range of values found for the corresponding Pt(II)–S examples, 2.27–2.35 Å, and the Au–S–C angle of 96.7 ° is to the low end of the Pt–S–C range (95.0–109.9 °). In contrast, the Au–O distance (2.076 Å), the S···O bite distance (3.077 Å), the Au–O–C angle (127.6 °) and the S–Au–O angle (89.8 °) are all in the middle of the equivalent ranges for the platinum examples [2]. So, other than a possibly slightly stronger, more-acute bonding of the S atom, the attachment of the thiosalicylate ligand to the (tolylpyridine)Au(III) fragment is very similar to that found for a variety of $L_2Pt(II)$ groups, emphasising the isoelectronic relationships.




**8a**, R = H
**8b**, R = Me

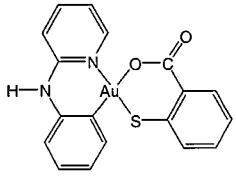



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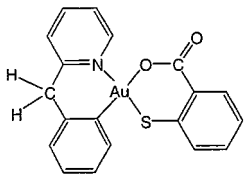
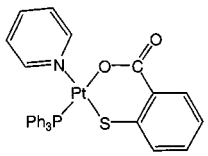
Table 2
Antitumour (P388) assay results for gold(III) thiosalicylate complexes

| Complex | $IC_{50}$ [a] | |
|---|---|---|
| | ng $ml^{-1}$ | μM |
| **8a** | 10 672 | 20.7 |
| **8b** | 1310 | 2.5 |
| **9** | 9181 | 17.7 |
| **10** | >62 500 | >120.6 |

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




**10**

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### 2.3. Biological activity

Activity data (against P388 leukaemia cells) for the various thiosalicylate complexes are summarised in Table 2. The tolylpyridine derived complex **8b** has good activity, but the other complexes have either moderate (**8a** and **9**) or poor activity (**10**).

## 3. Experimental

### 3.1. General experimental details

$^1$H-NMR spectra were recorded in $CDCl_3$ on Bruker AC300P spectrometer at 300.13 MHz. IR spectra were recorded as KBr discs on a BioRad FTS40 spectrometer, and melting points were determined using a Reichert Hotstage apparatus, and are uncorrected. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, or at the Chemistry Department, NUS.

ES mass spectra were obtained in positive-ion mode using a VG Platform II mass spectrometer. The compounds were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mM, and spectra were recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer via a Rheodyne injector fitted with a 10 μl sample loop. A ThermoSeparation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 ml $min^{-1}$, and nitrogen was employed both as a drying and nebulising gas. Cone voltages were varied from 20 to 200 V, in order to investigate the effect of higher voltages on fragmentation of parent ions. Confirmation of all species in this study was aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the ISOTOPE computer program [21].

The gold–dihalide complexes **4a** [11], **5** [13], and **6** [14] were prepared by the literature procedures. The compounds 2-(*p*-tolyl)pyridine (Aldrich), and thiosalicylic acid (Sigma) were used as supplied. Other chemicals used were at least of reagent grade.

### 3.2. Synthesis of complex 7

A solution of 2-(*p*-tolyl)pyridine (192 mg, 1.13 mmol) in MeCN (3 ml) was added to an aqueous solution (30 ml) of $HAuCl_4.xH_2O$ (340 mg, 1.0 mmol), and the solution allowed to stand overnight. The yellow crystals were filtered, washed with water and dried in vacuo to give **7** (343 mg, 73%). Anal. Found: C, 30.3; H, 2.2; N, 3.0. $C_{12}H_{11}NAuCl_3$ requires C, 30.5; H, 2.35; N, 3.0%. M.p. 159–162 °C. ESMS (MeCN–$H_2O$, cone voltage 20 V), [2-(*p*-tolyl)pyridine + H]$^+$ (*m*/*z* 170, 100%). IR: $\nu_{max}$ 1602, 1478, 770 $cm^{-1}$.

### 3.3. Synthesis of complex 4b

A suspension of complex **7** (345 mg, 0.73 mmol) in aqueous MeCN (1:1, 40 ml) was heated to reflux for 6 h, during which time a pale yellow solid formed. The solid was filtered from the hot mixture, and air-dried to give **4b** as a pale yellow fluffy solid (115 mg, 38%). Anal. Found: C, 32.9; H, 1.05; N, 2.9. Calc. for $C_{12}H_{10}NAuCl_2$: C, 33.1; H, 2.3; N, 3.2%. M.p. decomp. >260 °C. ESMS (MeCN–$H_2O$, cone voltage 50 V), [2-(*p*-tolyl)pyridine + H]$^+$ (*m*/*z* 170, 90%), [M − Cl + $NH_3$]$^+$ (*m*/*z* 417, 90%), [M − Cl + MeCN]$^+$ (*m*/*z* 441, 100%), plus several unidentified ions; (cone voltage 50 V, pyridine added), [M − Cl + pyridine]$^+$ (479, 100%).

### 3.4. Synthesis of complex 8a·1.5$H_2O$

Complex **4a** (844 mg, 2.00 mmol) was dissolved in acetone (30 ml) and silver nitrate (680 mg, 4.00 mmol) added. The mixture was stirred in the dark for 1 h and the silver chloride filtered off. The colourless filtrate was treated with thiosalicylic acid (308 mg, 2.00 mmol) and NaOH (160 mg, 4.00 mmol) in water (2 ml). The solution was filtered and the volume reduced at reduced pressure until crystallisation was just observed. Bright yellow crystals of **8a** were obtained from vapour diffusion of $Et_2O$ into an acetone solution. Yield 300 mg

(28%). M.p. softens >150 °C, m.p. 220–222 °C (decomp.). Anal. Found: C, 40.3; H, 2.4; N, 2.7; Au, 37.6. Calc. for $C_{18}H_{12}AuNO_2S$: C, 43.0; H, 2.4; N, 2.8%. Calc. for $C_{18}H_{15}AuNO_{3.5}S$: C, 40.8; H, 2.8; N, 2.6; Au, 37.1%. ESMS (MeCN–$H_2O$, cone voltage 50 V), $[M+H]^+$ ($m/z$ 504, 100%), $[2M+H]^+$ ($m/z$ 1007, 30%), $[2M+Na]^+$ ($m/z$ 1029, 5%).

### 3.5. Synthesis of complex *8b*

A mixture of the complex **4b** (95 mg, 0.23 mmol) and thiosalicylic acid (34 mg, 0.22 mmol) in MeOH (3 ml) with $Et_3N$ (three drops) was refluxed for 20 min, giving a clear yellow solution. Water (5 ml) was added, and the yellow microcrystalline product filtered and washed with water (5 ml), and dried in vacuo. The complex was dissolved in $CH_2Cl_2$ and filtered through a Pasteur pipette containing a plug of glass wool, which removed some dark, insoluble impurities. Vapour diffusion of $Et_2O$ into the $CH_2Cl_2$ solution gave bright yellow needles, and some dark powdery material; the latter was removed by several cycles of washing with $Et_2O$ and decantation. Yield 76 mg, 68%. Anal. Found: C, 44.2; H, 2.4; N, 2.6. Calc. for $C_{19}H_{14}NAuSO_2$: C, 44.1; H, 2.7; N, 2.7%. M.p. decomp. >224 °C. IR: $\nu$(CO) 1636 $cm^{-1}$ (vs). ESMS (MeCN–$H_2O$, cone voltage 50 V) $[M+H]^+$ ($m/z$ 518, 100%).

### 3.6. Synthesis of complex *9*

To a stirred yellow suspension of complex **5** (500 mg, 1.14 mmol) and thiosalicylic acid (185 mg, 1.20 mmol) in MeOH (40 ml) was added $Et_3N$ (2 ml, excess), which resulted in the formation of a lighter yellow cloudy solution, which rapidly deposited bright yellow microcrystals. After stirring in the dark for 30 min the mixture was cooled in ice, the solid filtered, washed with water (10 ml) and $Et_2O$ (10 ml) and dried in vacuo to give complex **9** (506 mg, 85%). M.p. decomp. >210 °C. Anal. Found: C, 41.7; H, 2.6; N, 5.3. Calc. for $C_{18}H_{13}N_2AuO_2S$: C, 41.7; H, 2.5; N, 5.4%. ESMS (MeCN–$H_2O$, cone voltage 50 V), $[M+H]^+$ ($m/z$ 519, 100%), $[2M+H]^+$ ($m/z$ 1037, 20%). The complex is only slightly soluble in $CH_2Cl_2$.

### 3.7. Synthesis of complex *10*

To a white suspension of complex **6** (400 mg, 0.917 mmol) in MeOH (30 ml) was added thiosalicylic acid (200 mg, 1.299 mmol) giving a yellow suspension. Triethylamine (1 ml, excess) was added to the stirred mixture, giving a deep yellow cloudy solution which rapidly deposited lemon yellow microcrystals. The mixture was stirred in the dark for 1 h, and water (40 ml) added to complete precipitation. The solid was filtered, washed with water (2 × 10 ml) and $Et_2O$ (2 × 10 ml), and dried to give complex **10** (330 mg, 69%). ESMS (MeOH, cone voltage 20V), $[M+H]^+$ ($m/z$ 518, 80%), $[M+Na]^+$ ($m/z$ 540, 55%), $[M+Na+MeOH]^+$ ($m/z$ 572, 20%), $[2M+H]^+$ ($m/z$ 1035, 80%), $[2M+Na]^+$ ($m/z$ 1057, 100%), $[3M+Na]^+$ ($m/z$ 1574, 85%). Cone voltage 80V, $[M+H]^+$ ($m/z$ 518, 18%), $[M+Na]^+$ ($m/z$ 540, 32%), $[M+Na+MeOH]^+$ ($m/z$ 572, 6%), $[2M+H]^+$ ($m/z$ 1035, 5%), $[2M+Na]^+$ ($m/z$ 1057, 100%), $[3M+Na]^+$ ($m/z$ 1574, 21%). The complex is soluble in $CH_2Cl_2$. A sample for elemental analysis was recrystallised by diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of the complex and found to crystallise with 0.25 molecules of $CH_2Cl_2$ per molecule of complex, from integration of the $^1$H-NMR spectrum. Anal. Found: C, 41.9; H, 2.6; N, 2.5; S, 6.0. Calc. for $C_{19}H_{14}NSAuO_2 \cdot 0.25CH_2Cl_2$: C, 42.9; H, 2.7; N, 2.6; S, 5.95%, m.p. loses solvent >150 °C, melts 207–209 °C (decomp.). $^1$H-NMR, $\delta$ 9.16–7.12 (m, Ph), 5.29 (s, $CH_2Cl_2$), 4.25 (s, br, $CH_2$).

### 3.8. Crystallography

Crystals of **8b** were obtained by diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of the complex at room temperature. Data were collected on a Siemens SMART CCD system with graphite-monochromated Mo–$K_\alpha$ radiation, and were corrected semi-empirically for absorption using SADABS [22]. The structure was solved by automatic interpretation of a Patterson map and developed routinely. In the final cycles of least-squares refinement (based on $F^2$ against all data) all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in their calculated positions.

#### 3.8.1. Crystal data

$C_{19}H_{14}AuNO_2S$, $M_r$ 1517.34, monoclinic, space group $C2/c$, $a = 22.3191(4)$, $b = 10.3556(2)$, $c = 13.6885(1)$ Å, $\beta = 92.626(1)$ °, $U = 3160.47(9)$ Å$^3$, $D_{calc} = 2.175$ g $cm^{-3}$, $Z = 8$, $F(000)$ 1968, $\mu$(Mo–$K_\alpha$) 9.453 $mm^{-1}$. Crystal size 0.55 × 0.06 × 0.06 mm.

A total of 9778 reflections were collected at 203(2) K in the range 1.83 to 27.48°, corresponding to 3497 unique data ($R_{int} = 0.0221$), $T_{max,min}$ 0.6584 and 0.3719. The refinement converged with $R_1 = 0.0202$, $wR_2 = 0.0499$ (for data with $I > 2\sigma(I)$), and $R_1 = 0.0241$, $wR_2 = 0.0519$, goodness-of-fit 1.109 (all data). The largest features in a final difference map were +1.230 and −1.467 e Å$^{-3}$.

### 3.9. Antitumour assays

Assays were carried out by the Marine Chemistry Group, University of Canterbury, Christchurch, New Zealand. All samples were dissolved in 3:1 MeOH–dichloromethane, in which they were soluble, and a two-fold dilution series of the initial 5 mg $ml^{-1}$ solu-

tion incubated for 72 h with the test cells. $IC_{50}$ values were determined by measurement of the absorbance values when the yellow dye MTT tetrazolium is reduced by healthy cells to the purple MTT formazan. Mitomycin C was included in the assays as a positive control.

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159578 for compound **8b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank the University of Waikato and the National University of Singapore (grant RP970614) for financial support of this work. Grants-in-aid from the New Zealand Lottery Grants Board towards the purchase of the electrospray mass spectrometer and gold are appreciated. W.H. thanks Amu Upreti and Wendy Jackson for technical assistance. We thank Allen Oliver and Associate Professor Cliff Rickard (University of Auckland) for X-ray data set collection.

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