Supplementary Information

Novel N-heterocyclic ylideneamine gold(I) complexes: synthesis, characterisation and screening for antitumour and antimalarial activity

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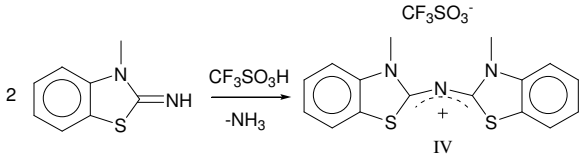
Synthesis and characterisation of 3-methyl-2-(3-methyl-3*H*-benzothiazol-2-ylideneamino)benzothiazol-3-ium trifluoromethanesulfonate, IV

During the preparation of 3-methyl-3*H*-benzothiazol-2-ylideneamine (**II**, see main text), reaction temperatures above 66 ºC led to the formation of the dimeric byproduct 3-methyl-2-(3-methyl-3*H*-benzothiazol-2-ylideneamino)benzothiazol-3-ium trifluoromethanesulfonate, **IV**. This compound is propsosed to form *via* a condensation reaction which entails the loss of ammonia (Scheme SI 1) and similar compounds have been prepared by Deligeorgiev and Gadjev[1] by treating 3-methyl-3*H*-benzothiazol-2-ylideneamine derivatives with HX, where X = $CH_3SO_3^-$, ClO_4^-, Br^- or I^-.



Scheme SI 1 Proposed formation of **IV**

The byproduct **IV**, crystallised from a dichloromethane solution of compound **II** as yellow needles in the monoclinic space group $P2_1/c$, with two unique molecules of **IV** and one dichloromethane molecule present in the asymmetric unit. Fig. SI 1 depicts the molecular structure, indicating the numbering scheme, and Table SI 1 summarises selected bond lengths and angles of only one of the symmetrically unique molecules of **IV** as the bond lengths and angles in the two molecules do not differ significantly. The similarity between the C(1)–N(1)/C(1)–N(2) and C(3)-N(9)/C(9)-N(2) bond lengths and their intermediate value when typical double C=N and single C–N bond distances are considered, suggest stabilisation of the positive charge by extensive delocalisation of the π-electron density in the formal double and single bond over these bonds. Other bond parameters in the two 5-membered heterocyclic rings such as S–C–S angles and C–S bond distances do not differ significantly from each other and the heterocyclic rings in 2-ylideneamine compounds.

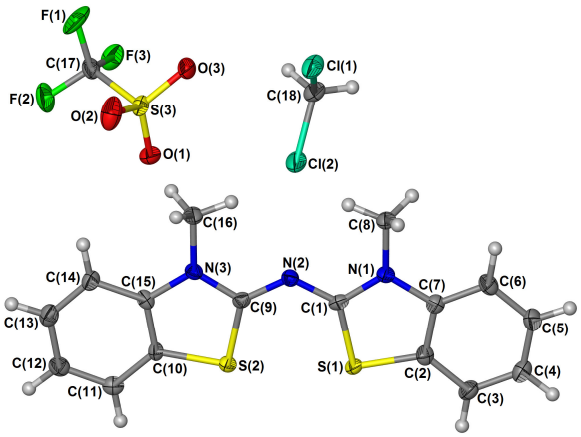


Fig. SI 1 Molecular structure of a unique molecule of **IV** in the asymmetric unit (thermal ellipsoids are drawn at 50% probability level).

In the solid state packing of **IV** the cations assemble in columns which are stabilised by π-π interactions between the neighbouring benzimidazole rings. (Fig. SI 2). Additionally, numerous weak hydrogen bonds such as C-H…O, C-H…N, C-H…F involving counterions and solvent molecules further stabilise the packing.

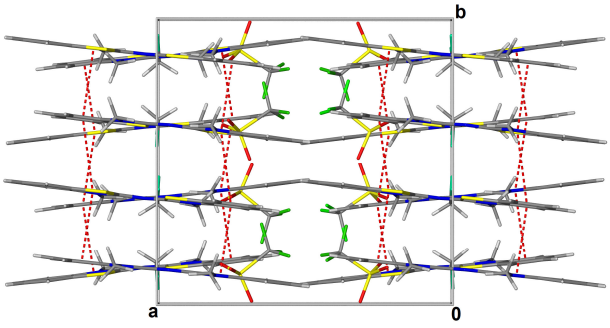


Fig. SI 2 Solid state packing of **IV** viewed along the c-axis, showing the columnar criss-cross packing motif of the 3-methyl-2-(3-methyl-3*H*-benzothiazol-2-ylideneamino)benzothiazol-3-ium cations stabilised by π-π interactions (in orange).

Table SI 1 Selected bond lengths (Å) and angles (°) of **IV** with estimated standard deviations in parenthesis

Bond lengths/Å		*Bond angles/°*	
N(2)–C(1)	1.324(6)	C(1)–N(2)–C(9)	124.2(4)
N(2)–C(9)	1.324(6)	N(1)–C(1)–N(2)	118.8(4)
N(1)–C(1)	1.350(6)	N(3)–C(9)–N(2)	120.1(4)
N(3)–C(9)	1.358(6)	N(2)–C(1)–S(1)	129.9(4)
N(1)–C(7)	1.414(6)	N(2)–C(9)–S(2)	129.0(4)
N(3)–C(15)	1.389(6)	N(1)–C(1)–S(1)	111.3(3)
N(1)–C(8)	1.465(6)	N(3)–C(9)–S(2)	110.9(4)
N(3)–C(16)	1.469(6)	C(1)–N(1)–C(7)	114.6(4)
S(1)–C(1)	1.749(5)	C(9)–N(3)–C(15)	114.8(4)
S(2)–C(9)	1.749(5)	C(1)–S(1)–C(2)	91.2(2)
S(1)–C(2)	1.743(5)	C(9)–S(2)–C(10)	91.3(2)
S(2)–C(10)	1.752(5)	N(1)–C(7)–C(2)	111.7(4)
C(2)–C(7)	1.398(7)	N(3)–C(15)–C(10)	112.9(4)
C(15)–C(10)	1.401(7)	S(1)–C(2)–C(7)	111.2(4)
		S(2)–C(10)–C(15)	110.1(4)

Molecular Structure of 4a

The poor crystal quality of **4a** resulted in weak X-ray diffraction data and is therefore included in the SI merely for the purpose of comparison. The presence of included solvent molecules influence the solid state packing immensely. The appearance of π-π interactions between the neighbouring benzimidazole rings, absent in **4b**, as well as numerous, new, weak C-H…O interactions between the triphenylphosphine unit and nitrate ion are noteworthy.

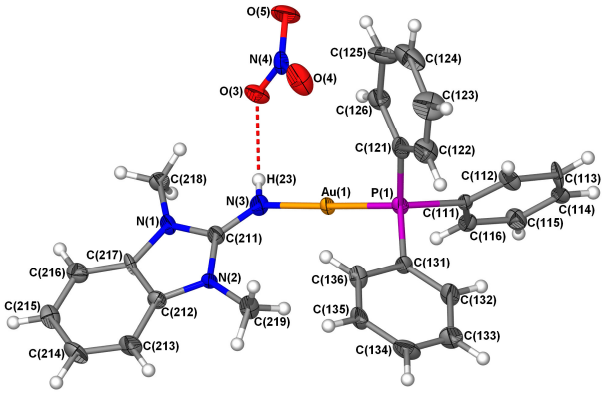


Fig. SI 3 Molecular structure of **4a** showing the numbering scheme (thermal ellipsoids drawn at 50% probability level).

Table SI 3 Selected bond lengths (Å) and angles (°) of **4a** with estimated standard deviations in parenthesis

Bond lengths/Å	*Bond angles/°*
Au(1)–P(1) 2.226(3)	N(3)–Au(1)–P(1) 177.0(3)
Au(1)–N(3) 2.031(9)	C(211)–N(3)–Au(1) 131.3(8)
N(3)–C(211) 1.297(15)	N(1)–C(211)–N(3) 126.0(11)
N(1)–C(211) 1.378(14)	N(2)–C(211)–N(3) 126.9(11)
N(2)–C(211) 1.353(14)	N(1)–C(211)–N(2) 107.1(10)
N(1)–C(218) 1.438(14)	
N(2)–C(219) 1.454(14)	

To improve the refinement stability, restraints were placed on the displacement parameters of the atoms C(1), C(2), C(3), and O(1) of one acetone molecule. A restraint on the bond length C(2)-C(3) was also applied.

Table SI 2 Crystallographic data collection parameters of **4a**

Compound reference	**4a**
Chemical formula	$C_{33}H_{38}AuN_4O_5P$
Formula Mass	798.61
Crystal system	Triclinic
a/Å	9.043(3)
b/Å	14.043(4)
c/Å	14.902(4)
α/°	63.333(4)
β/°	85.257(4)
γ/°	84.437(4)
Unit cell volume/Å^3	1681.5(8)
Temperature/K	150(2)
Space group	$P\bar{1}$
No. of formula units per unit cell, *Z*	2
No. of reflections measured	18785
No. of independent reflections	7599
R_{int}	0.0878
Final R_1[a] values ($I > 2\sigma(I)$)	0.0869
Final wR_2[b] values ($I > 2\sigma(I)$)[a]	0.1701
Final R_1[a] values (all data)	0.1191
Final wR_2[b] values (all data)	0.1828
Goodness-of-fit	1.140

[a] $R_1 = \Sigma[\|F_o\| - |F_c\|/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Notes and references

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1 T. Deligeorgiev, N. I. Gadjev, *Dyes and Pigments* 1995, **29**, 315.