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# 5,6-Dicyano-2,3-dithiopyrazine (dcdmp) chemistry: synthesis and crystal structure of Au(III)(dcdmp)<sub>2</sub> complexes and 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene

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## Abstract

As an effort to explore new complexes of the 2,3-dicyano-5,6-dimercaptopyrazyne (dcdmp) ligand with different transition metals, different salts containing both the Au(dcdmp)<sub>2</sub><sup>-</sup> complex and the new species 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene (tctata), were obtained and characterized. *n*-Bu<sub>4</sub>N Au(dcdmp)<sub>2</sub> crystallises in monoclinic space group C2/c, Z = 8 with unit cell parameters a = 35.147(4), b = 9.527(1), c = 21.792(2) Å and  $\beta = 109.626(8)^{\circ}$ . Its crystal structure consist of almost regular columns of [Au(dcdmp)<sub>2</sub>]<sup>-</sup>, stacked along *b*, surrounded by *n*-Bu<sub>4</sub>N<sup>+</sup> cations. *n*-Bu<sub>4</sub>N AuBr<sub>2</sub> (tctata) crystallises in triclinic space group  $P\overline{1}$ , Z = 2, with unit cell parameters a = 10.986(1), b = 13.230(2), c = 13.791(1) Å,  $\alpha = 79.150(9)^{\circ}$ ,  $\beta = 69.663(6)^{\circ}$ ,  $\gamma = 70.254(9)^{\circ}$ . The crystal packing is made by zig-zag chains of tctata separated by layers of cations, with AuBr<sub>2</sub> anions located in alternated cavities between the tctata chains and the cation layers. At last, *n*-Bu<sub>4</sub>N[Au(dcdmp)<sub>2</sub>] (tctata) crystallises in monoclinic space group  $P2_1/n$ , Z = 4, with unit cell parameters a = 10.693(2), b = 40.308(7), c = 10.870(1) Å,  $\beta = 92.16(1)^{\circ}$ . Its crystal structure can be seen has a mix of those of the two preceding compounds. It consists of bidimensional layers of [nBu<sub>4</sub>N]<sup>+</sup>. In the last two compounds the tctata and [Au(dcdmp)<sub>2</sub>]<sup>-</sup> units. The adjacent layers are separated by layers of [nBu<sub>4</sub>N]<sup>+</sup>. In the last two compounds the tctata appears as a planar molecule.

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# 1. Introduction

Transition metal bisdithiolene complexes have, since their earlier studies during the sixties, attracted a great interest due to a rich variety of coordination geometry, and vivid redox behaviour [1]. These characteristics made them as choice building blocks for molecular materials displaying unconventional electrical and magnetic properties [2]. One of the key aspects in the versatility of these complexes, making them so attractive in the design of magnetic properties of molecular materials, is that both by change in the transition metal and in the oxidation state they can display different magnetic moments.

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Square planar coordination geometry with these ligands is frequently observed in the anionic form with metals of Ni and Cu groups and such complexes have been used as counterions in charge transfer solids with a variety of donors. This planar geometry often favours solid state structures presenting more or less regular staking of the planar units providing chains of extended interactions in the solid, which can give rise to interesting properties such as ferromagnetism [3], metallic conductivity [4] or even superconductivity [5,6].

In these type of complexes both the accessibility to different oxidation states and the magnitude of the solid state interactions is expected to be favoured by ligands with more extended  $\pi$ -systems. While sulfur rich ligands have been extensively explored significantly less effort has been devoted to the study of other extended dithiolene  $\pi$ -ligands containing different heteroatoms like

N and O. These heteroatoms are expected to act also as an extra coordinating site which may provide an additional degree of freedom in crystal engineering of these solids, as recently demonstrated for pyrazinediselenate [7] and pyrazinedithiolate [8] Cu complexes. With the 2,3-dicyano-5,6-dimercaptopyrazyne (dcdmp) ligand the only reported complexes previously to our work are with nickel in the monoanionic form, Ni(dcdmp)<sub>2</sub><sup>-</sup> [9] and with it a few charge transfer salts with TTF and other related donors have been also described.

Preliminary data on charge transfer salts of  $Au(dcdmp)_2^-$  with TTF type donors were previously reported by us [10]. In this paper we report the synthesis and characterization of the  $Au(dcdmp)_2^-$  complex, and we describe two salts containing the new species 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene (tctata) obtained as the product of a side reaction between the ligand with its precursor.

#### 2. Experimental

# 2.1. Synthesis

To a suspension of sodium sulfate monohydrated in acetone (241 mg,  $1 \times 10^{-3}$  mol) was added, under stirring, an acetone solution of 2,3-dichloro-5,6-dicianopyrazine (100 mg,  $5.02 \times 10^{-4}$  mol). The formed red solution was filtered and added to a solution (2 ml) of potassium tetrachloroaurate (95 mg,  $2.51 \times 10^{-4}$  mol) in acetone, turning to a brown mixture. The inorganic precipitate was removed and the liquor added to 1 ml of a solution of tetrabutylammonium bromide (81 mg,  $2.51 \times 10^{-4}$  mol) in acetone, giving rise to an orangegold solution. The stirring was maintained, in all steps, until no visible modification was observed. This solution was then filtered and allowed to a slow evaporation of the solvent in inert atmosphere. The orange solid obtained was filtered and recrystallised in acetonediethyl ether, to afford needle shape crystals with three different colours. There are red (3) and yellow (4) crystals dominating the sample, but some green (5) crystals can be found also. In all cases, the crystals were suitable for X-ray diffraction measurements, revealing three different compositions. Visual separation of the crystals afforded the following characterisation data.

**3**: Tetrabutylammonium salt of gold(III)-bis-5,6dicyano-2,3-dithiopyrazine, *n*-Bu<sub>4</sub>N Au(dcdmp)<sub>2</sub>, m.p. 258.3–260.5 °C (followed by decomposition). IR (KBr):  $\tilde{V} = 434$  (w, Au–S), 735 (m, CH<sub>2</sub>–S–CH<sub>2</sub>), 1172 (S, C– N), 1266 (m), 1301 (S), 1455 (m), 1481 (w, C=N–C), 2233 (m, C=N), 2879–2966 (m, C–H alifat) cm<sup>-1</sup>. UV– Vis (CH<sub>3</sub>CN):  $\lambda_{max} = 1413$ , 1721, 1911, 2275, 2496 nm. *Anal.* Calc. for CHNS (C<sub>28</sub>H<sub>36</sub>N<sub>9</sub>S<sub>4</sub>Au): C, 40.82; H, 4.40; N, 15.30; S, 15.56. Found: C, 42.38; H, 3.70; N, 15.64; S, 15.71%. MS: m/z (%) 580.9 [M<sup>-</sup>] (100) [C<sub>12</sub>N<sub>8</sub>S<sub>2</sub>Au], 242.3 [M<sup>+</sup>] (100) [C<sub>16</sub>H<sub>36</sub>N].

4: Tetrabutylammonium salt of gold dibromide with 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene, *n*-Bu<sub>4</sub>N AuBr<sub>2</sub> (tctata), m.p. 189.2–191.3 °C (followed by decomposition). IR (KBr):  $\tilde{V} = 428$  (S, Au–Br), 742 (m, CH<sub>2</sub>–S–CH<sub>2</sub>), 884 (m), 1170 (S, C–N), 1235 (m), 1325 (S), 1381 (m), 1485 (m, C=N–C), 1507 (m), 2240 (w, C=N), 28877–2966 (m, C–H alifat) cm<sup>-1</sup>. UV–Vis (CH<sub>3</sub>CN):  $\lambda_{max} = 1413$ , 1721, 1911, 2275, 2496 nm. *Anal.* Calc. for CHNS (C<sub>28</sub>H<sub>36</sub>N<sub>9</sub>S<sub>2</sub>AuBr<sub>2</sub>): C, 36.57; H, 3.94; N, 13.71; S, 6.97. Found: C, 38.54; H, 3.61; N, 14.04; S, 6.68%. MS: *m/z* (%) 288.0 (100) [C<sub>12</sub>N<sub>8</sub>S<sup>-</sup>], 250.0 (39) [C<sub>12</sub>N<sub>7</sub>S<sup>-</sup>], 356.8 (28) [AuBr<sub>2</sub><sup>-</sup>], 197.0 (100) [Au<sup>+</sup>], 242.3 (78) [C<sub>16</sub>H<sub>36</sub>N<sup>+</sup>].

**5**: Tetrabutylammonium salt of gold(III)-bis-5, 6-dicyano-2,3-dithiopirazine with 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthrene, n-Bu<sub>4</sub>N[Au(dcdmp)<sub>2</sub>] (tcta-ta): the isolated amount of this compound was not enough to any characterization further than its structure determined by X-ray diffraction.

## 2.2. X-ray structure determination

The data collection was performed on two different Enraf-Nonius CAD4 diffractometer, one equipped with graphite monochromatised Mo  $K\alpha$  radiation а  $(\lambda = 0.71069 \text{ A})$  and the other equipped with a graphite monochromatised Cu K $\alpha$  radiation ( $\lambda = 1.54150$  A), in the  $\omega - 2\theta$  scan mode. The structures were solved by direct methods using SIR97 [11] and refined by fullmatrix least-squares methods using the program SHELXL97 [12] and the WINGX software package[13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP3 [14] and SCHAKAL-97 [15]. Crystal data and structure refinement of are summarized in Table 1.

### 3. Results and discussion

## 3.1. Synthesis

The synthesis of the gold complex **3** was performed following a standard procedure for the preparation of dithiolates from dichlorides, (Scheme 1) also used to prepare the Ni analogue [9]. The dithiolate ligand (**2**) in solution was obtained from the corresponding chloride salt (**1**) by treatment with Na<sub>2</sub>S, in acetone. This ligand, without intermediate isolation was successively reacted with potassium tetrachloroaurate and *n*-Bu<sub>4</sub>NBr, also in acetone solutions, followed by slow evaporation of the solvent in inert atmosphere, to give the gold(III) complex that was obtained as a red needle

Table 1 Crystallographic data for compounds **3**, **4** and **5** 

Compound	3	4	5
Crystal size (mm)	$0.70 \times 0.32 \times 0.14$	0.7  imes 0.3  imes 0.2	$0.50 \times 0.25 \times 0.14$
Crystal system	monoclinic	triclinic	monoclinic
Crystal color/shape	red/needle	yellow/needle	green/needle
Space group	C2/c	$P\overline{1}$	$P2_1/n$
Lattice constants (Å, °)	a = 35.147(4)	a = 10.986(1)	a = 10.693(2)
	b = 9.527(1)	b = 13.230(2)	b = 40.308(7)
	c = 21.792(2)	c = 13.791(1)	c = 10.870(1)
		$\alpha = 79.150(9)$	
	$\beta = 109.626(8)$	$\beta = 69.663(7)$	$\beta = 92.16(1)$
		$\gamma = 70.254(9)$	
Volume (Å <sup>3</sup> )	6873.3(1)	1763.3(3)	4682(1)
Formula sum	$C_{28}H_{36}AuN_9S_4$	$\mathrm{C}_{28}\mathrm{H}_{36}\mathrm{Au}\mathrm{Br}_{2}\mathrm{N}_{9}\mathrm{S}_{2}$	$C_{40}H_{36}AuN_{17}S_6$
Formula weight	823.86	919.56	1144.18
Ζ	8	2	4
$\rho_{calc}$ (Mg/m <sup>3</sup> )	1.592	1.732	1.623
Absorption coefficient (mm <sup>-1</sup> )	4.557	6.588	8.824
F(000)	3280	896	2280
Wavelength	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)	Cu Ka (1.54150 Å)
<i>T</i> (K)	273(2)	293(2)	293(2)
$\theta$ range (°)	2.22-26.00	2.07-26.03	4.28-72.87
Index range $(h, k, l)$	-43/40, 0/11, 0/26	-12/13, -16/16, 0/16	-12/0, 0/48, -12/12
Scan type	$\omega - 2\theta$	$\omega - 2 heta$	$\omega - 2\theta$
Number of collected reflections	6906	7136	8842
Number of unique reflections/ $R_{int}$	6718/0.0756	6840/0.0211	8425/0.1277
$T_{\rm max}$ and $T_{\rm min}$	0.9975/0.4966	0.9864/0.7158	
Goodness-of-fit on $F^2$	0.901	1.045	1.017
Number of refined parameters	379	379	578
R (observed reflections)	0.0666	0.0669	0.0684
$wR_2$ (observed reflections)	0.1047	0.1480	0.1582





shaped crystals. The elemental analysis is consistent with a 1:1 stoichiometry, as confirmed by the X-ray crystal structure determination. Unexpectedly two other different kind of complexes were obtained, n-Bu<sub>4</sub>N[Au(dcdmp)<sub>2</sub>] (tcdpdt) (4), as yellow needles and n-Bu<sub>4</sub>NAuBr<sub>2</sub>(tcdpdt) (5) as green needle shaped crystals, both containing the new species (tctata) (6). The structures of 3, 4 and 5 were solved by single crystal X-ray diffraction (Scheme 1).

The unprecedented formation of the tetracyanotetraazathianthrene 6 incorporated in the structure of 4 and 5, can be explained by a side reaction, taking place between the starting dichloride 1 and the dithiolate ligand 2. The dithiolate acts as a nucleophilic agent, and substitutes the chlorine atoms in the pyrazine ring through an aromatic nucleophilic substitution mechanism which is activated by the cyano groups and further helped by the presence of the nitrogen atoms in the aromatic ring. Both the cyano groups and the nitrogen atoms are electroattractors, enhancing an electronic deficiency on the carbon atoms linked to chlorine (Scheme 2).

This explanation is supported by the fact that the above proposed reaction is similar to that previously



Scheme 2.

used to prepare other thiantrenes [16,18], but wewere not successful in isolating 6 as a pure compound.

Cyclic voltammetry of *n*-Bu<sub>4</sub>NAu(dcdmp)<sub>2</sub> (3) in acetonitrile (Fig. 1, full line) shows a pair of symmetric reversible redox waves at  $E_{1/2} = -0.629$  V vs Ag/AgCl ascribed to the couple Au(dcdmp)<sub>2</sub><sup>2-</sup>/Au(dcdmp)<sub>2</sub><sup>-</sup>. The cyclic voltammetry of **4** in the same conditions (Fig. 1, dashed line) shows three irreversible waves at -0.604, -0.349 and +0.732 V. The last wave is close to the values reported for the reaction AuBr<sub>2</sub><sup>-</sup>  $\leftrightarrow$  Au+2Br<sup>-</sup> [17] but the two first waves are ascribed to tcata.

# 3.2. Structural characterisation

The crystal quality made possible to solve the crystal structure of compounds **3**, **4** and **5**. The geometry of the Au(dcdmp)<sub>2</sub><sup>-</sup> complex in **3** and **5** is identical, with average Au–S bond lengths of 2.307(3) and 2.320(3) Å, respectively (see Table 2). These values are in the upper side of the range of values reported for other gold(III) dithiolates that extend from 2.29 to 2.34 Å, with an average value of 2.305 Å. In both cases the complex is almost planar, with significant non planar deviations



Fig. 1. Cyclic voltammetry of n-Bu<sub>4</sub>N[Au(dcdmp)<sub>2</sub>] (solid line) and n-Bu<sub>4</sub>N(tctata)AuBr<sub>2</sub> (dashed line), in acetonitrile.

Table 2												
Selected	bond	lengths	(Å)	of	[Au(	(dcdmp)	2]-	complexes	in	3	and	5

	3	5
Au1–S1	2.303(3)	2.314(3)
Au1–S2	2.309(3)	2.322(3)
Au1–S3	2.303(3)	2.325(3)
Au1–S4	2.313(3)	2.317(3)
S1-C1	1.72(1)	1.73(1)
S2-C2	1.73(1)	1.73(3)
S3-C7	1.73(1)	1.72(1)
S4–C8	1.74(1)	1.72(1)
C1–C2	1.47(1)	1.44(1)
C7–C8	1.43(1)	1.45(1)
C1-N1	1.32(1)	1.35(1)
C2-N2	1.32(1)	1.34(1)
C7-N5	1.30(1)	1.34(1)
C8–N6	1.32(1)	1.32(2)
N1-C3	1.32(1)	1.34(1)
N2-C4	1.33(1)	1.34(1)
N5-C9	1.35(1)	1.31(2)
N6-C10	1.34(1)	1.34(1)
C3–C4	1.42(1)	1.37(1)
C9-C10	1.40(1)	1.39(2)
C3–C5	1.42(2)	1.41(2)
C4–C6	1.44(2)	1.45(2)
C9-C11	1.50(2)	1.43(2)
C10-C12	1.47(2)	1.45(2)
C5–N3	1.16(2)	1.14(2)
C6-N4	1.12(2)	1.16(2)
C11-N7	1.11(2)	1.14(2)
C12–N8	1.17(2)	1.14(2)

observed only in the terminal cyano groups, which are displaced towards opposite directions giving rise to a very small chair type distortion (Figs. 2 and 3). In both complexes the dcdmp ligands are identical within experimental uncertainty and with a geometry close to that found in the corresponding Ni analogue [9].

The new tetracyanothianthrene tctata species, present in complexes 4 and 5, has bond lengths and angles identical to the corresponding ones in the dcdmp ligand in the dithiolates and an almost planar geometry in good agreement with that found in the unsubstituted analogue tetraazothiaantrene [18] (Figs. 3 and 4, Table 3). The two tctata molecules in 4, are identical with an almost planar geometry, with a small twist of the terminal cyano groups, in opposite directions. The angles of the central ring range from 126.1° to 127.9°, in the case of the C=C-S angles, and show the values of 105.6° and 105.9° for the C-S-C angle. In the crystal structure of 5, the tctata molecule shows a slight deviation from pla-



Fig. 2. ORTEP views and atomic numbering scheme of  $Au(dcdmp)^{2-}$ , in **3**, with thermal ellipsoids at 40% probability.

narity. There is a significant deviation of the sulphur atom, relatively to the average plane of the molecule and therefore the dihedral angle between the two half of the molecule is  $174^{\circ}$ . The non planarity is also denoted by the central ring bond angles that in the case of C=C-S bonds range from  $125.5^{\circ}$  to  $126.6^{\circ}$  while those of the C-S-C bonds are  $107.7^{\circ}$  and  $106.3^{\circ}$ . The deviation of the S atoms from the average molecular plane is certainly due to short contacts between these atoms and gold and carbon atoms in neighbouring ditiolate species (see Table 6).

To the best of our knowledge tctata, together with bis(quinoxaline)-2,2',3,3'-disulfide [19] and 1,4,6,9-tetraazathianthrene [18], are the only azathiaantrenes displaying an essentially planar geometry, while all others present significant molecular dihedral angles ranging from 132° to 143°.

The tetrabutylammonium salt 3, crystallises in the monoclinic system, space group C2/c, Z = 8. The unit cell contains one independent [Au(dcdmp)<sub>2</sub>]<sup>-</sup>complex and one independent tetrabutylammonium cation in general positions. The crystal structure consists of columns of  $[Au(dcdmp)_2]^-$  pairs, stacked along b (Fig. 5). The normal to complex plane makes an angle of 51.6° with this axis. There are two different overlap modes between complexes characterised by a different displacement along their long axis. The distance between the average plane of  $[Au(dcdmp)_2]^-$  complexes are almost identical, being 3.49 and 3.47 A, between and within the pairs of dithiolates, respectively. The stacks of the complexes are completely surrounded by  $[n-Bu_4N]^+$ cations which prevent any contact between neighbouring stacks (Fig. 6).

The adopted overlap mode between stacked complexes at such a short distance corresponds to the existence of several short interatomic contacts (see Table 4),



Fig. 3. ORTEP views and atomic numbering scheme of tctata units in 4, with thermal ellipsoids at 40% probability.



Fig. 4. ORTEP views and atomic numbering scheme of  $Au(dcdmp)^{2-}$  (a) and tctata (b), in 5, with thermal ellipsoids at 40% probability.

Table 3 Selected bond lengths (Å) of **6** in **4** and **5** 

	5	<b>4</b> mol1	<b>4</b> mol2
S01-C01	1.75(2)	1.758(8)	
S01-C07	1.74(1)	1.732(9)	
S02-C02	1.75(1)		1.74(1)
S02-C08	1.74(1)		1.72(1)
C01-N01	1.31(2)	1.29(1)	
C07-N05	1.31(1)	1.31(1)	
C02-N02	1.30(1)		1.30(1)
C08-N06	1.31(1)		1.33(1)
C01-C02	1.45(1)		
C07–C08	1.45(1)		
C03-N01	1.32(2)	1.35(1)	
C09-N05	1.33(1)	1.35(1)	
C04-N02	1.38(2)		1.33(1)
C010-N06	1.32(1)		1.32(1)
C04-C03	1.37(2)		
C010-C09	1.40(2)		
C03-C05	1.50(2)	1.47(2)	
C09-C011	1.42(2)	1.44(1)	
C04-C06	1.41(2)		1.44(1)
C010-C012	1.44(2)		1.42(2)
C05-N03	1.13(2)	1.17(2)	
C011-N07	1.14(2)	1.11(1)	
C06-N04	1.16(2)		1.12(1)
C012-N08	1.14(2)		1.19(2)



Fig. 5. Partial views of the crystal structure of **3** (a) view showing the short contacts between molecules along the dithiolate columns: the shortest contacts (dotted line) and contacts exceeding no more than 4% the sum of the van der Waals radii (dashed line); (b) view along *c*, showing the relative positions of dithiolates in two columns.



Fig. 6. View of the crystal structure of 3 along b.

Table 4									
Hydrogen	bonds	and	short	contacts	in	the	crystal	structure	of <b>3</b>

	d (Å)	Angle (°)	$d$ (Å)/ $\Sigma r_{\rm vdw}$
$Au \cdot \cdot \cdot S4$	3.688		0.89
$Au \cdots N2$	3.576		0.94
Au···C2	3.824		0.98
Au···C8	3.768		0.97
S1···H23a–C23	2.961	161.56	0.97
S4···H24a–C24	3.026	132.78	0.99
N3···H44a–C44	2.589	173.05	0.96
Au···Au	4.630		1.01
$Au \cdot \cdot \cdot S2$	4.202		1.03
Au···N6	3.960		1.04
$Au \cdot \cdot \cdot C4$	3.965		1.02

 $\Sigma r_{\rm vdw} =$  van der Waals radii sum

some clearly below the sum of van der Waals radii (dotted lines in Fig. 5), the shortest one being  $Au \cdots S1$  (3.71 Å). Other interactions are noticed slightly above the sum of van der Waals radii, as  $Au \cdots Au$  exceeding by 1% that sum (dashed line in Fig. 5).

The interactions between the dithiolate complexes and the tetrabuthylamonium cations are established though several hydrogen bonds (Fig. 7, Table 4), only one through a pyrazinic nitrogen atom. Clearly the crystal structure of **3** is determined by the short complex interactions through both Au–S and Au–Au contacts and  $\pi$ - $\pi$  interactions between ligands.

Compound 4 crystallises in the triclinic system, space group  $P\bar{1}, Z = 2$ . The unit cell has two independent units of tctata located at inversion centres, one independent tetrabutylamonium cation and one independent AuBr<sub>2</sub> anion. The crystal packing is made by zig-zag chains of tctata, separated by layers of the tetrabutylammonium cations parallel to the *b*, *a*-*c* plane (Fig. 8). The tctata units along the chains are connected by short S···S



Fig. 7. Hydrogen bonds between the dithiolate anions and neighbouring cations, in the crystal structure of **3**.



Fig. 8. (a) View of the crystal structure of 4 along *b*. (b) Partial view of the tctata zig-zag chains emphasising the  $S \cdots S$  short contact, along the chain.

contacts at 3.586 Å and the angle between the average planes of these species is 76.1°. The AuBr<sub>2</sub>units, with a linear geometry typical of monoanionic state, are located in alternated cavities between the totata chains and cationic planes (Fig. 9). There are several short contacts ( $\approx 4$  Å) between the gold atom and the sulphur atoms of

a c c

Fig. 9. Partial view of the crystal structure of 4, showing the short contacts between the different species.

Table 5 Hydrogen bonds and short contacts in the crystal structure of **4** 

	d (Å)	Angle (°)	
C51–H51a···N04	2.551	152	
C31-H31b···S02	2.943	149	
C21–H21a···Au	3.291	145	
C24–H24b···Au	3.247	163	
$Au \cdot \cdot \cdot S02$	4.026		
Au···S01	3.924		
$S01 \cdots S02$	3.586		

the tctata unit and hydrogen bonds between the Au atom and the surrounding tetrabuthylamonium cations (see Table 5). The interactions between the tctata units and the tetrabuthylamonium cation are made through several hydrogen bonds (Table 5, Fig. 9), none of them involving the pyrazinic nitrogen atoms.

The last salt, 5, crystallises in the monoclinic system, space group  $P2_1/n$ , Z = 4. The unit cell contains one independent molecule of tctata, one independent tetrabutylamonium cation and one independent [Au(dcdmp)<sub>2</sub>]<sup>-</sup> complex all located in general in general positions. Its crystal structure can be seen as a combination of those of the two preceding compounds. It consists of bidimensional layers, in the a, c plane, composed of out of registry parallel zig-zag chains of alternating totata and  $[Au(dcdmp)_2]^-$  units (Fig. 11). The adjacent layers are separated by cation layers  $[nBu_4N]^+$ , along b, (Fig. 10). Several short contacts, within layer, can be noticed. With exception of the  $S3 \cdots S3$  interaction between the anions in neighbouring



Fig. 10. View of the crystal structure of 5 along a.



Fig. 11. View of the tctata and  $[Au(dcdmp)_2]^-$  layer, in the *a*, *c* plane, in the crystal structure of **5**, emphasising the short contact responsible for the bidimensional network.

Table 6 Hydrogen bonds and short contacts in the crystal structure of **5** 

	<i>d</i> (Å)	Angle (°)
C-H13a···N6	2.641	159.83
C–H14e···N7	2.633	174.50
C-H13b···N07	2.503	154.04
Au···S01	4.004	
Au···S02	3.730	
Au…N01	4.041	
Au···N06	3.648	
S3···S3	3.664	
S01···C9	3.380	
S02···C9	3.431	



Fig. 12. Hydrogen bonds between the tctata and  $[Au(dcdmp)_2]^-$  molecules and neighbouring cations, in the crystal structure of **5**.

chains, all short contacts are between different species and involve the sulphur atom of the neutral complex and the carbon atom of the pyrazine ring in the anion. The short contacts along the chain are of the Au···S type and the angle between the units is  $62.7^{\circ}$  (Fig. 11, Table 6). The neutral tctata and the Au(dcdmp)<sub>2</sub><sup>-</sup> anions in the layer are connected with the tetrabutylammonium through C–H···N hydrogen bonds. The nitrogen atoms involved in this interaction, are available both from the anion and the neutral specie (Fig. 12, Table 6), only one trough the pyrazinic N6 atom. The crystal structure of this compound is dominated by strong interactions between tctata and Au(dcdmp)<sub>2</sub><sup>-</sup> involving S–S and S–Au contacts as in **3** which determine the formation of layers.

#### 4. Conclusion

In conclusion the  $Au(dcdmp)_2$  complex was prepared and the structure of two salts described in detail. Although tetracyanotetraazothianthrene could no be isolated as a pure compound, two salts containing this new thianthrene derivative were obtained. In both cases this thianthrene derivative presents an almost planar geometry.

At variance with other pyrazinediselenate [7] or pyrazinedithiolate [8] salts where the N heteroatom acted as a new coordination centre in these compounds with the dicyanopyrazine ligand no such role is observed. However the pyrazinic ring contributes to electron delocalisation and allows  $\pi$ - $\pi$  interactions between ligands of different complexes.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre. The deposition numbers are CCDC 222525, CCDC 222526 and CCDC 222527 for compounds **3**, **4** and **5** respectively. Copies of the data can be obtained free of charge upon application to the director of CCDC, 12 Union Road, GB, Cambridge CB12 1EZ. [Fax: +441223/336/033, E-mail deposit@ccdc.cam.ac.uk, or on the web: http://www.ccdc.cam.ac.uk].

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