# THE PREPARATION OF MIXED-LIGAND DITHIOLENE COMPLEXES: X-RAY STRUCTURE OF Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(mnt) AND [Bu<sub>4</sub>N][Au(mnt)<sub>2</sub>]

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Abstract—Reaction of  $PtCl_2(PR_3)_2$  with sodium dithiolates gives mixed-ligand complexes such as  $Pt(PR_3)_2(mnt)$  (1). Attempts to prepare mixed S—N/mnt complexes of gold were unsuccessful,  $[Bu_4N][Au(mnt)_2]$  (2) being obtained. New compounds were characterized by IR and NMR spectroscopy and microanalyses, and in the case of 1 and 2 by X-ray crystallography. Both 1 and 2 are square planar. In 2, one of the crystallographically independent anions lies over a symmetry related neighbour.

Transition-metal dithiolene complexes have been of interest for a number of years as they have potential for conductivity in the solid state.<sup>1-5</sup> In general, bis complexes have been most studied since they are planar and resemble compounds used in organic metals [e.g. if a metal replaces the central ethylene group atoms in tetrathiofulvalene (TTF), M(dmit)<sub>2</sub> complexes are formed. Complexes containing the ligand dmit (4,5-dimercapto-1,3-dithiole-2-thione) and dddt (4,5-dihydro-1,4-dithiin-2,3-dithiolate) have a high structural resemblance to the bis (ethylenedithio)tetrathiafulvalene molecule (ET)]. Recently, we have prepared complexes of the type  $[Pt(S_2N_2H)(PR_3)_2]X$  and note that despite their lack of symmetry these materials stack in the solid state.<sup>6,7</sup> Here, we describe our investigations into the synthesis of mixed-ligand dithiolene complexes. The X-ray structures of Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(mnt) (1) and  $[Bu_4N][Au(mnt)_2]$  (2) are also reported.



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#### EXPERIMENTAL

General conditions and spectroscopic methods were as described previously.<sup>8</sup> Na<sub>2</sub>mnt,<sup>9</sup> Na<sub>2</sub>edt,<sup>10</sup> quinoxaline-2,3-dithiol (QDT),<sup>11</sup> S<sub>4</sub>N<sub>4</sub>H<sub>4</sub>,<sup>12</sup> [Me<sub>2</sub>SnS<sub>2</sub>N<sub>2</sub>]<sub>2</sub><sup>13</sup> and [Bu<sub>4</sub>N][Au(mnt)Br<sub>2</sub>]<sup>14</sup> were prepared as described in the literature. PtCl<sub>2</sub>(COD) was prepared from K<sub>2</sub>PtCl<sub>4</sub> and COD in the presence of SnCl<sub>2</sub>·2H<sub>2</sub>O.<sup>15</sup> Compounds of the type *cis*-PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> were made by adding stoichiometric amounts of the appropriate free phosphine to PtCl<sub>2</sub>(COD).

Electrochemical work was performed at ambient temperature and pressure using a Princeton Applied Research (PAR) Model 273 and peripheral equipment on solutions which were deoxygenated by purging with argon.  $[Bu_4N][PF_6]$  was prepared by mixing hot aqueous solutions of  $[Bu_4N]I$  and  $[NH_4][PF_6]$ ; the precipitate was recrystallized twice from methanol and vacuum dried at 100°C for 24 h. CH<sub>2</sub>Cl<sub>2</sub> (distilled from CaH<sub>2</sub>) was transferred to a voltammetry cell containing sufficient  $[Bu_4N][PF_6]$ and electroactive compound to make the solution ca 0.1 and  $5 \times 10^{-4}$  M in these compounds, respectively. All potentials are referred to the Ag/Ag<sup>+</sup> electrode. Preparation of  $Pt(PR_3)_2(mnt)$  (PR<sub>3</sub> = PEt<sub>3</sub>, PMe<sub>2</sub>Ph)

In a typical reaction, PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (70 mg, 0.129 mmol) was mixed with an equimolar amount of Na<sub>2</sub>mnt (24 mg, 0.129 mmol) and CH<sub>2</sub>Cl<sub>2</sub>-MeOH (20 cm<sup>3</sup>, 3:1). After 2 h, the orange-red solution was filtered and evacuated to dryness. The resulting solid was dissolved in  $CDCl_3$  (2–3 cm<sup>3</sup>). The orange solid was recrystallized from hot ethanol to give shiny pink microcrystals of Pt(PMe<sub>2</sub> Ph)<sub>2</sub>(mnt) (51 mg, 65%). Layering a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound with *n*-hexane gave crystals suitable for X-ray diffraction. Found: C, 39.2; H, 3.5; N, 4.3. Calc. for Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(mnt): C, 39.3; H, 3.6; N, 4.3%.  ${}^{31}P{}^{1}H{}$  (ppm):  $\delta$  -19.34(s)  ${}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P})$  2778 Hz;  ${}^{1}\text{H}$  (ppm):  $\delta$  1.71 (s, 12H, Me)  ${}^{2}J({}^{31}P_{-1}H)$  10 Hz  ${}^{3}J({}^{195}Pt_{-1}H)$  29 Hz, 7.38 (m, 10H, Ph) o 7.35, p 7.39, m 7.42. IR (cm<sup>-1</sup>): 2222m, 2205vs, 1492vs, 1436vs, 1420vs, 1385s, 1287m, 1154s, 1107vs, 946vs, 924vs, 851m, 807w, 741vs, 719vs, 691vs, 508w, 482s, 445m, 434m, 372w.

Pale pink crystals were obtained for the PEt<sub>3</sub> derivative. Found : C, 33.6; H, 5.2; N, 4.8. Calc. for Pt(PEt<sub>3</sub>)<sub>2</sub>(mnt) : C, 33.6; H, 5.3; N, 4.9%. <sup>31</sup>P{<sup>1</sup>H} (ppm) :  $\delta$  4.82(s) <sup>1</sup>J(<sup>195</sup>P—<sup>31</sup>P) 2749 Hz, <sup>1</sup>H (ppm) :  $\delta$  1.12 (t, 3H, Me) <sup>3</sup>J(CH<sub>2</sub>—CH<sub>3</sub>) 8 Hz <sup>3</sup>J(<sup>31</sup>P—<sup>1</sup>H) 16 Hz, 2.05 (m, CH<sub>2</sub>) with Pt—H and P—H couplings. IR (cm<sup>-1</sup>): 2221m, 2202vs, 1497vs, 1453s, 1416m, 1384m, 1260m, 1152s, 1110m, 1035vs, 1011m, 870w, 804w, 768s, 752vs, 745s, 726s, 701m, 629m, 508m, 441m, 426m, 387w, 310w.

# **Preparation** of $Pt(PR_3)_2(edt)$ (PR<sub>3</sub> = PEt<sub>3</sub>, PMe<sub>2</sub>Ph)

Na2edt (27 mg, 0.2 mmol) was added to a stirred solution of PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> (100 mg, 0.2 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>). An immediate yellow coloration resulted. After 2 h, the solution was filtered and evacuated to dryness. The <sup>31</sup>P{<sup>1</sup>H} NMR revealed two peaks with accompanying Pt-P splittings; that of the desired product and the starting phosphine ( $\delta$  9.13 ppm, <sup>1</sup>J 3513 Hz). Evaporation of the solvent to ca 0.5 cm<sup>3</sup> resulted in the formation of white needle-shaped crystals. Yield 55 mg (57%). Found: C, 32.1; H, 6.0. Calc. for Pt(PEt<sub>3</sub>)<sub>2</sub>(edt): C, 32.2; H, 6.2%.  ${}^{31}P{}^{1}H{}$  (ppm):  $\delta$  4.35(s),  ${}^{1}J({}^{195}Pt-{}^{31}P)$  2732 Hz. IR (cm<sup>-1</sup>): 1523m, 1453m, 1415m, 1384m, 1376m, 1103w, 1033vs, 811s, 767vs, 760vs, 725vs, 675vs, 634m, 417m, 354w, 325w, 292w.

Addition of diethyl ether was required to precipitate the PMe<sub>2</sub>Ph derivative as a yellow solid (63 mg, 61%). Found: C, 37.9; H, 4.2. Calc. for Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(edt): C, 38.5; H, 4.3%. <sup>31</sup>P{<sup>1</sup>H} (ppm):  $\delta - 19.00(s) {}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}) 2722 \text{ Hz. IR}$ (cm<sup>-1</sup>): 1519w, 1475w, 1434m, 1417m, 1400m, 1312w, 1262w, 1155w, 1103vs, 945s, 905vs, 853w, 839w, 808m, 758m, 748s, 734s, 716m, 697s, 667s, 482m, 447m, 432m, 374w, 366w, 337w, 328w.

# Preparation of $Pt(PR_3)_2(QDT)$ (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PEt<sub>3</sub>)

To a stirred solution of QDT (30 mg, 0.154 mmol) in MeOH (5 cm<sup>3</sup>) was added sodium (10 mg, 0.435 mmol). After 10 min, PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> was added together with  $CH_2Cl_2$  (5 cm<sup>3</sup>) and the resulting solution was stirred for 2 h. Evaporation of the solvent to 5 cm<sup>3</sup> and addition of Et<sub>2</sub>O resulted in precipitation of the orange complex. Found: C, 43.1; H, 3.9; N, 4.2. Calc. for Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(QDT): C, 43.4; H, 3.9; N, 4.2%.  ${}^{31}P{}^{1}H{}$  (ppm):  $\delta$ -17.9(s) <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 2835 Hz. IR (cm<sup>-1</sup>): 1547m, 1482w, 1434m, 1414m, 1387w, 1356m, 1328w, 1313w, 1259s, 1172vs, 1121vs, 1105s, 1049w, 1024w, 948s, 907vs, 843w, 805w, 762m, 743m, 717m, 689m, 599m, 489m, 445m, 428m. PEt<sub>3</sub> derivative: Found: C, 38.1; H, 5.4; N, 4.4. Calc. for Pt(PEt<sub>3</sub>)<sub>2</sub>(QDT): C, 38.5; H, 5.5; N, 4.5%.  ${}^{31}P{}^{1}H{}$  (ppm):  $\delta$  5.5(s)  ${}^{1}J{}^{195}Pt{}^{-31}P{}$  2817 Hz. IR (cm<sup>-1</sup>): 1550m, 1480w, 1458m, 1453m, 1417m, 1370w, 1365m, 1254s, 1179vs, 1123vs, 1038vs, 1025s, 1004m, 802w, 768vs, 757vs, 726vs, 638m, 598m, 444m, 426m.

# Reaction of $[Bu_4N][Au(mnt)Br_2]$ with $S_4H_4N_4/dbu$

 $[Bu_4N][Au(mnt)Br_2]$  (59.2 mg,  $8.01 \times 10^{-5}$  mol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) to which was added S<sub>4</sub>N<sub>4</sub>H<sub>4</sub> (7.5 mg,  $4.0 \times 10^{-5}$  mol) and an excess of dbu (~ 5 drops). The solution darkened to an orange-brown colour. After filtration, the solvent was reduced *in vacuo* to 0.5 cm<sup>3</sup>. Dark red crystals were formed. Found : C, 39.5; H, 5.0; N, 9.6. Calc. for  $[Bu_4N][Au(mnt)_2]$ : C, 40.0; H, 5.0; N, 9.7%. Mass spectrometry: M<sup>-</sup> (FAB): 477 Au(mnt)<sub>2</sub><sup>-</sup>.

Reaction of  $[Bu_4N][Au(mnt)Br_2]$  with  $[Me_2SnS_2N_2]_2$ 

 $[Bu_4N][Au(mnt)Br_2]$  (87 mg, 0.105 mmol) and  $[Me_2SnS_2N_2]_2$  (28.3 mg,  $5.25 \times 10^{-5}$  mol) were combined in degassed CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>). After 24 h, the yellow-brown solution was filtered through celite and reduced to ~ 5 cm<sup>3</sup> in vacuo. Ether was added slowly until a dark brown, crystalline solid was deposited. Recrystallization from acetone-EtOH followed by slow hexane diffusion into a dichloromethane solution of the compound gave dark red crystals which analysed as  $[Bu_4N][Au(mnt)_2]$ .

### Crystal data

C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>P<sub>2</sub>PtS<sub>2</sub> (1), M = 611.6, triclinic, a = 9.22(5), b = 11.318(6), c = 11.552(7) Å,  $\alpha = 84.02(4)$ ,  $\beta = 84.64(4)$ ,  $\gamma = 71.73(4)^{\circ}$ , U = 1149Å<sup>3</sup>, space group PĪ, Z = 2,  $D_c = 1.77$  g cm<sup>-3</sup>. Pink, air-stable prisms,  $\alpha$ (Cu-K<sub>w</sub>) = 146 cm<sup>-3</sup>,  $\lambda = 1.54178$  Å, F(000) = 592. C<sub>24</sub>H<sub>36</sub>AuN<sub>5</sub>S<sub>4</sub> (2), M = 719.8, triclinic, a = 13.405(5), b = 13.533(5), c = 17.612(5) Å,  $\alpha = 75.98(3)$ ,  $\beta = 79.92(3)$ ,  $\gamma = 78.37(3)^{\circ}$ , U = 3009 Å<sup>3</sup>, space group PĪ, Z = 4(two crystallographically independent molecules),  $D_c = 1.59$  g cm<sup>-3</sup>,  $\mu$ (Cu-K<sub>a</sub>) = 120 cm<sup>-1</sup>,  $\lambda = 1.54178$  Å, F(000) = 1432.

### Data collection and processing

Nicolet R3m diffractometer,  $\omega$ -scan method ( $\theta \leq 50$  and 58°, respectively), graphite monochromated Cu- $K_{\alpha}$  radiation; for 1 2662 and for 2 8126 independent measured reflections, 2559 and 6&83 observed [] $F_{\alpha} > 3\sigma$ {] $F_{\alpha}$ ]), corrected for Lorentz and polarization factors; empirical absorption corrections based on 343 and 360 azimuthal measurements. Maximum and minimum transmission factors for 1 were 0.602 and 0.17, and for 2 0.131 and 0.042, respectively.

### Structure analysis and refinement

Complex 1 was solved by the heavy atom method and 2 by direct methods; in both cases all the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were idealized (C-H = 0.96 Å), assigned isotropic thermal parameters U(H) = 1.2Ueq(C) and allowed to ride on their parent carbons. In 2 the methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix leastsquares to R = 0.040  $(R = \Sigma_{i})F_{a} - F_{a})/\Sigma_{i}F_{a}$  $R_{\rm w} = 0.042 \; ({\rm w}^{-1} = \sigma^2(F) + 0.0010F^2)$  for 1, and to  $R = 0.050, R_w = 0.55 (w^{-1} = \sigma^2(F) + 0.00144F^2)$ for 2. The maximum and minimum residual electron densities in the final  $\Delta F$  maps were 1.67, 1.25 and -1.07, -1.77 eÅ<sup>-3</sup>, and the mean and maximum shifts/error in the final refinement cycle were 0.002, 0.008 and 0.018, 0.048, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.<sup>16</sup>

### **RESULTS AND DISCUSSION**

In the light of the observed stacking properties in  $[Pt(S_2N_2H)(PR_3)_2]X$ , we have prepared mixedligand complexes containing dithiolenes and phosphines as well as studying methods for the preparation of complexes containing dithiolenes and SN ligands. Reaction of PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> with the sodium salt of the appropriate dithiolene ligand (mnt, edt, QDT) gives the desired mixed-ligand complex in fair yield. The new compounds gave satisfactory microanalyses and had the expected spectroscopic properties. Their <sup>31</sup>P NMR spectra consist of singlets with platinum satellites (<sup>3</sup> $J(^{31}P-^{183}Pt) ca$ 2800 Hz).



The IR spectra are as expected.<sup>17</sup> In the case of the mnt complexes the v(C = N) and v(C - C)vibrations increase in frequency by *ca* 10 and 55 cm<sup>-1</sup>, respectively, upon complexation indicating a decrease in bond length, whilst the  $v(C - S)_{sym}$ vibration is reduced in frequency consistent with lengthening of the C—S bonds.

We have also attempted to prepare mixed dithiolene/SN complexes of gold. Thus reaction of  $S_4N_4H_4$  or  $[Me_2SnS_2N_2]_2$  with  $[Bu_4N]$  $[Au(mnt)Br_2]$  was carried out by analogy with previous routes to  $S_2N_2^{2-}$  complexes.<sup>6-8</sup> In both cases we observed formation of  $[Bu_4N][Au(mnt)_2]$ (2) rather than the desired complex. Complex 2 has previously been obtained<sup>18</sup> from the reaction of auric acid and Na<sub>2</sub>mnt.

A number of the compounds prepared have been studied by cyclic voltammetry. The cyclic voltammogram for Au(mnt)<sub>2</sub><sup>-/</sup>/CH<sub>2</sub>Cl<sub>2</sub> was found to contain oxidative and reductive one electron reversible couples at  $E_{1/2(\text{oxid})} = +1.15$  V and  $E_{1/2(\text{red})} = -0.88$  V. This compares with the results obtained by Schlupp and Maki<sup>19</sup> for Au(mnt)<sub>2</sub><sup>-/</sup> DMSO ( $E_{1/2(\text{red})} = -0.41$  V vs SCE).

Gold(III) is isoelectronic with platinum(II)  $(d^8)$ and it is probable that the gold and platinum mnt complexes have similar electronic structures. Schlupp and Maki have calculated that in the formal gold(III) complex  $Au(mnt)_2^{\lambda_-}$   $(d^8)$  the electron is largely based on the ligand orbital (80%  $A_g$  character). Geiger *et al.*<sup>20</sup> have noted the difficulty in assigning Pt(mnt)<sub>2</sub><sup>3-</sup> as platinum(I) (isoelectronic with Au(mnt)<sub>2</sub><sup>2-</sup>) and have concluded that reduction of the platinum(II) complex could be either metal or ligand based. This is also likely for Au(mnt)<sub>2</sub><sup>-</sup>.

The redox chemistry of  $M[S_2C_2Ph_2]_2$  (M = Ni, Pd, Pt)<sup>21</sup> and  $[M(S_2C_2Ph_2)(PPh_3)_2]$  (M = Pd, Pt) has been studied with the existence of the dithioketyl radical  $C_2S_2Ph_2^-$  characterized by ESR.



Fig. 1. The X-ray structure of 1.



Fig. 2. The X-ray structure of 2.

Reversible oxidation is found to occur on the dithiolene ligand and is relatively independent of the metal atom or phosphine. In the case of  $Pt(PR_3)_2(mnt)$  studied here we observed irreversible oxidative peaks at +1.25 V indicating a secondary process (e.g. ligand dissociation).

The X-ray structures of  $Pt(PMe_2Ph)_2(mnt)$  (1) and  $[Bu_4N][Au(mnt)_2]$  (2) are shown in Figs 1 and 2, with selected bond lengths and angles in Tables 1 and 2. Complex 1 has the expected square-planar geometry with approximate non-crystallographic  $C_2$  symmetry. There is a characteristic slight enlargement of the P—Pt—P angle (92.4(1)°) as a consequence of the bulk of the phosphine ligands. The Pt—P and Pt—S bond lengths are typical for platinum(II). The Pt—S bond length in 1 is slightly longer than in Pt(mnt)<sub>2</sub><sup>-</sup>,<sup>4</sup> reflecting the difference

in the *trans* effect of sulphur versus phosphorus rather than the difference in formal oxidation state. The transannular  $S \cdots S$  distance is 3.23 Å. In 2 there are two crystallographicaly independent molecules. There are no significant differences in their geometries; both anions having approximate non-crystallographic  $D_{2h}$  symmetry. The bond lengths and angles are within statistical significance identical to those reported<sup>22</sup> for [Au(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub>][Au(mnt)<sub>2</sub>]. Replacement of platinum by gold does not appear to have any effect on the M—S distance in complexes of this type.<sup>4,22</sup> The transannular  $S \cdots S$  distance in 2 (3.27 Å) is essentially identical to the cis inter-ring S...S distance (3.28 Å) underlining that  $mnt^{2-}$  is an almost optimum chelating ligand for the formation of undistorted bis complexes.

Pt—S(1)	2.309(2)	Pt—S(4)	2.301(2)
Pt - P(1)	2.278(2)	PtP(2)	2.289(2)
S(1)—C(2)	1.715(8)	P(1) - C(11)	1.828(7)
P(1)C(17)	1.824(9)	P(1)-C(18)	1.818(13)
P(2)—C(21)	1.819(8)	P(2)—C(27)	1.809(8)
P(2)—C(28)	1.817(12)		
S(1)—Pt—S(4)	88.8(1)	S(1)—Pt—P(1)	89.5(1)
S(4) - Pt - P(1)	178.3(1)	S(1)—Pt—P(2)	178.1(1)
S(4)P(2)	89.2(1)	P(1)PtP(2)	92.4(1)
Pt—S(1)—C(2)	102.7(3)	S(1)C(2)C(3)	124.1(6)
S(1) - C(2) - C(4)	117.4(7)	C(3) - C(2) - C(4)	118.5(7)
C(2) - C(3) - S(4)	120.9(6)	C(2)-C(3)-C(5)	121.6(8)
S(4) - C(3) - C(5)	117.5(8)	Pt—S(4)—C(3)	103.5(3)
C(2) - C(4) - N(4)	178.6(10)	C(3)—C(5)—N(5)	179.1(9)

Table 1. Selected bond lengths (Å) and angles (°) in 1

Au(1)—S(2)	2.308(3)	2.304(3)
Au(1)—S(6)	2.300(3)	2.312(2)
Au(1) - S(1)	2.307(3)	2.306(3)
Au(1)-S(5)	2.309(3)	2.309(3)
S(1) - C(1)	1.749(10)	1.731(10)
C(1)—C(3)	1.424(15)	1.453(13)
C(2) - C(4)	1.389(14)	1.421(16)
C(4) - N(4)	1.142(14)	1.162(18)
C(5)—C(6)	1.351(15)	1.336(13)
C(6)—S(6)	1.746(10)	1.707(9)
C(7)—N(7)	1.148(14)	1.160(14)
S(1)—Au(1)—S(2)	90.4(1)	90.6(1)
S(2)—Au(1)—S(5)	178.9(1)	179.6(1)
S(2)—Au(1)—S(6)	88.6(1)	90.1(1)
Au(1) - S(1) - C(1)	101.1(4)	100.1(3)
S(1) - C(1) - C(3)	115.3(9)	114.7(7)
C(1) - C(2) - S(2)	122.8(7)	122.7(8)
S(2) - C(2) - C(4)	114.8(9)	116.9(8)
C(1) - C(3) - N(3)	179.1(10)	177.2(12)
Au(1) - S(5) - C(5)	101.1(4)	100.5(3)
S(5)—C(5)—C(7)	116.6(8)	115.1(7)
C(5)-C(6)-S(6)	122.9(7)	124.2(7)
S(6)-C(6)-C(8)	114.4(8)	117.3(7)
S(1) - Au(1) - S(5)	90.6(1)	89.2(1)
S(1) - Au(1) - S(6)	178.9(1)	177.1(1)
S(5) - Au(1) - S(6)	90.4(1)	90.0(1)
S(1) - C(1) - C(2)	124.1(7)	125.6(7)
C(2) - C(1) - C(3)	120.5(9)	119.6(9)
C(1) - C(2) - C(4)	122.3(10)	120.3(9)
Au(1) - S(2) - C(2)	101.5(4)	100.8(3)
C(2)—C(4)—N(4)	176.4(12)	177.9(14)
S(5)-C(5)-C(6)	124.4(7)	124.1(7)
C(6)—C(5)—C(7)	119.0(9)	120.8(9)
C(5)-C(6)-C(8)	122.7(9)	118.5(8)
Au(1)-S(6)-C(6)	101.1(4)	101.1(3)

Table 2. Selected bond lengths (Å) and angles (°) for the two independent molecules in 2

In 1 there are no close contacts and there is no evidence of any intermolecular stacking. In 2 there are no significant intermolecular interactions between the crystallographically independent anions (the planes of the anions are inclined  $ca 64^\circ$ ). However, centrosymmetrically related pairs of one of the anions pack parallel to each other (Fig. 3) with an interplanar separation of 3.7 Å; the C(5)— C(6) bond lying almost directly over, and parallel



Fig. 3. Line drawing of the packing of centrosymmetrically related anions in **2**.

to, the  $S(5)'' \cdots S(6)''$  transannular vector of the symmetry related anion.

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