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Gold complexes with 2-selenoxo-1,3-dithiole-4,5-dithiolato

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Abstract—The reaction of Na_2dmise (dmise = 2-selenoxo-1,3-dithiole-4,5-dithiolate) with [AuClL] in 1 : 2 molar ratio affords $[Au_2(dmise)L_2]$ (L = PR_3 or CH_2PPh_3) but in 1 : 1 ratio in the presence of (NBu_4) Br gives (NBu_4)[Au(dmise)L]. The PPh_2Me dinuclear derivative further reacts with $[Au(OClO_3)(PPh_2Me)]$ to give $[Au_3(dmise)(PPh_2Me_3)_3]ClO_4$. The reaction with $[Au_2(P\text{-}P)Cl_2]$ renders $[Au_2(P\text{-}P)(dmise)]_n$ with different nuclearity depending on the diphosphine used (P-P = dppe, $n = 1$; dppm, $n = 2$). Anionic derivatives $(PPN)_2[Au_2(dmise)(C_6F_5)_2]$ and $(PPN)[Au(dmise)_2]$ are obtained by reaction with the corresponding halo-anionic gold complexes. © 1997 Elsevier Science Ltd

Keywords: gold; dithiolate; dmise; phosphine; ylide.

The ligands dmit (2-thioxo-1,3-dithiole-4,5-dithiolate), dmise (2-selenoxo-1,3-dithiole-4,5-dithiolate) and analogues have been shown a considerable interest as versatile building blocks of conducting materials [1–6]. Since several examples of $M(dmit)_2$ salts with intramolecular S···S interactions *via* terminal thioxo group have been found [7], a selenoxo group is expected to increase these terminal contacts owing to the more diffuse and spatially extended orbitals of selenium compared with sulphur. Few studies on dmise ligand have been reported to date, in particular $[M(dmise)_2]^{n-}$ (M = Ni, Pd $n = 1$–2) [5,8] derivatives and only two of them have shown a metallic behaviour [1,9].

In this paper we report a study of co-ordination properties of dmise ligand with gold derivatives leading to complexes in which the dmise is acting as bidentate chelate $\{(NBu_4)[Au(dmise)L]$ and $(PPN)[Au(dmise)_2]\}$ among others with novel coordination modes as bridge μ_2 $\{[Au_2(dmise)L_2]$ (L = phosphine), $[Au_2(dmise)(L\text{-}L)]_n$ (L-L = dppm, dppe) or $(PPN)_2[Au_2(dmise)(C_6F_5)_2]\}$ and μ_3 $\{[Au_3(dmise)L_3]ClO_4\}$.

EXPERIMENTAL

General procedures

Infrared spectra were recorded on a Perkin Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets, ^1H and ^{31}P NMR spectra on a Varian UNITY 300 in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^1H) and H_3PO_4 (external ^{31}P). The C, H, N and S analyses were performed with a Perkin Elmer 2400 microanalyser. Conductivities were measured in acetone with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS + or −) using nitrobenzylalcohol as matrix. The yields C, H, N and S analyses and $^{31}P\{^1H\}$ and some ^1H NMR data are listed in Table 1.

Starting materials

4,5-Bis(benzoylthio)-1,3-dithiole-2-selenone [1,8(c)] $[AuCl(PR_3)]$ [15], $[AuCl(CH_2PR_3)]$ [16], $Q[Au(C_6F_5)X]$ [15], $[Au_2(\mu\text{-dppm})Cl_2]$ [17] and $[Au_2(\mu\text{-dppe})Cl_2]$ [17] were obtained according to the literature procedures.

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Table 1. Analytical and spectroscopic data for complexes **1**–**12**

Complex	Yield (%)	Analysis: found (calc.) (%) C	H	S	N	^{31}P NMR (ppm)	^{1}H NMR δ_{Me} (J_{P-H})
1 $[Au_2(dmise)(PPh_3)_2]$	65	39.65	2.4	11.6	—	36 (s)	—
		(40.3)	(2.6)	(11.1)			
2 $[Au_2(dmise)(P(p\text{-}C_6H_4OMe)_3)_2]$	68	39.8	2.7	8.85	—	35 (s)	2.3 (s)
		(40.35)	(3.1)	(9.5)			
3 $[Au_2(dmise)(PPh_2Me)_2]$	65	33.5	1.9	13.0	—	20 (s)	2.07 (d, 10.2 Hz)
		(33.5)	(2.4)	(12.4)			
4 $[Au_2(dmise)(PMe_3)_2]$	60	14.4	2.5	17.3	—	−8.6 (s)	1.6 (d, 11.2 Hz)
		(13.7)	(2.3)	(16.3)			
5 $[Au_2(dmise)(CH_2PPh_3)_2]$	65	41.8	3.15	11.5	—	31 (s)	1.9 (d, 12.2 Hz)
		(41.4)	(2.85)	(10.8)			
6 $[Au_3(dmise)(PPh_2Me)_3]ClO_4$	60	32.2	2.0	9.2	—	18.2 (s, br)[a]	2.11 (d, 10.2 Hz)
		(32.9)	(2.5)	(8.3)			
7 $[Au_2(dmise)(dppe)]$	62	33.8	1.9	10.9	—	32.7 (s)	3.45 (s)
		(33.6)	(2.3)	(12.4)			
8 $[Au_4(dmise)_2(dppm)_2]$	63	32.55	2.1	13.0	—	37.5 (dd)	4.15 (m), 4.35 (m)
		(32.9)	(2.15)	(12.5)		24.1 (dd)	
9 $(NBu_4)[Au(dmise)(PPh_3)]$	60	46.6	5.05	14.4	1.2	42.5 (s)	—
		(47.0)	(5.4)	(13.6)	(1.5)		
10 $(NBu_4)[Au(dmise)(PPh_2Me)]$	65	42.95	5.0	15.0	1.3	23.5 (s)	2.1 (d, 8.5 Hz)
		(43.5)	(5.5)	(14.5)	(1.6)		
11 $(PPN)_2]Au_2(dmise)(C_6F_5)_2]$	70	50.5	3.1	6.7	1.1	—	—
		(51.0)	(2.45)	(6.3)	(1.35)		
12 $PPN[Au(dmise)_2]$	90	41.8	2.3	22.0	1.3	—	—
		(41.3)	(2.4)	(21.05)	(1.15)		

[a] At −60°C: 17.6 (s) and 19.3 (s).

Preparation of $[Au_2(dmise)(L)_2]$ [L = PPh_3 (**1**), $P(p\text{-}C_6H_4OMe)_3$ (**2**), PPh_2Me (**3**), PMe_3 (**4**), CH_2PPh_3 (**5**)].

Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-selenone (68 mg, 0.15 mmol) were dissolved under nitrogen atmosphere in methanol (20 cm^3) to give a dark red solution of Na_2dmise, to which was added $AuCl(PPh_3)$ (148 mg, 0.3 mmol), $AuCl(P(p\text{-}C_6H_4OMe)_3)$ (175 mg, 0.3 mmol), AuCl (PPh_2Me) (129 mg, 0.3 mmol), $AuCl(PMe_3)$ (93 mg, 0.3 mmol) or $AuCl(CH_2PPh_3)$ (152 mg, 0.3 mmol). Immediately different colour solid complexes (**1**–**5**) precipitated: dark yellow (**1**, **4**), brown (**2**, **3**) and orange (**5**), which were collected by filtration, washed with methanol and dried *in vacuo*.

Preparation of $[Au_3(dmise)(PPh_2Me)_3]ClO_4$ (**6**)

To a dichloromethane solution of $[AuCl(PPh_2Me)]$ (43 mg, 0.1 mmol) was added $AgClO_4$ (20 mg, 0.1 mmol). After stirring for 1 h the suspension was filtered through 1 cm of Celite, $[Au_2(dmise)(PPh_2Me)_2]$ (104 mg, 0.1 mmol) was added to the resulting solution. After stirring for 3 h the solution was concentrated by evaporation and the addition of diethyl ether led to precipitation of a dark garnet solid which was filtered off and dried *in vacuo*.

Preparation of $[Au_2(dmise)(L\text{-}L)]_n$ [n = 1, L-L = dppe (**7**), n = 2, L-L = dppm (**8**)]

To a methanolic solution (20 cm^3) with sodium metal and 4,5-bis(benzoylthio)-1,3-dithiole-2-selenone (68 mg, 0.15 mmol) under dinitrogen, was added $[Au_2(\mu\text{-dppe})Cl_2]$ (129 mg, 0.15 mmol) or $[Au_2(\mu\text{-dppm})Cl_2]$ (127 mg, 0.15 mmol). The solutions turn brown. After 1 h of stirring, the solutions were concentrated to dryness. Addition of acetone (20 cm^3) gave white solids corresponding to NaCl, which were filtered through 1 cm of Celite. Partial evaporation of the resulting solutions and addition of diethyl ether led to the precipitation of light brown solids which were filtered off and dried *in vacuo*.

Preparation of $NBu_4[Au(dmise)L]$ [L = PPh_3 (**9**), PPh_2Me (**10**)]

4,5-Bis-(benzoylthio)-1,3-dithiole-2-selenone (68 mg, 0.15 mmol) was dissolved under nitrogen atmosphere in a methanol (20 cm^3) solution containing sodium metal (9 mg, 0.4 mmol). A dichloromethane (5 cm^3) solution of $AuCl(PPh_3)$ (75 mg, 0.15 mmol) or $AuCl(PPh_2Me)$ (64 mg, 0.15 mmol) was added followed by a dichloromethane (5 cm^3) solution of NBu_4Br (48 mg, 0.15 mmol) with stirring. The solutions turned red. After stirring for 12 h the solutions were evaporated to remove all the solvent, and acetone (15 cm^3) was added affording a white solid corresponding to NaCl, which was filtered off. The solutions were concentrated to 5 cm^3. Addition of diethyl ether precipitated garnet solid, which was filtered off.

Preparation of $(PPN)_2[Au_2(dmise)(C_6F_5)_2]$ (11)

Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-selenone (68 mg, 0.15 mmol) were dissolved under nitrogen atmosphere in methanol (20 cm^3) to give a dark red solution, to which was added $PPN[Au(C_6F_5)Cl]$ (222 mg, 0.3 mmol). Immediately pink solid precipitated, which was collected by filtration, washed with methanol and dried *in vacuo*.

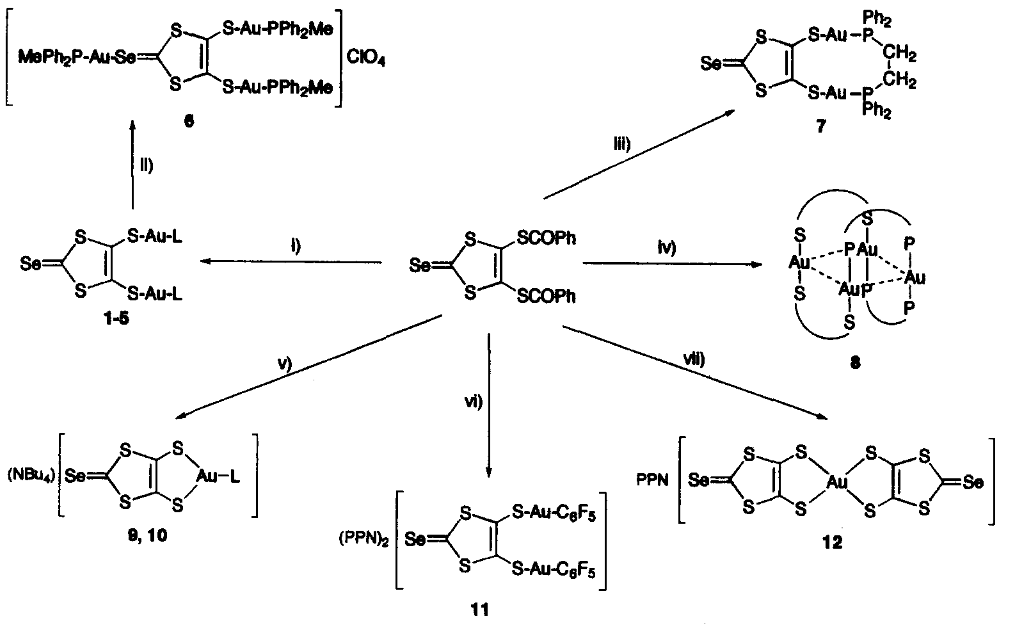
Preparation of $PPN[Au(dmise)_2]$ (12)

Sodium metal (9 mg, 0.4 mmol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-selenone (90 mg, 0.2 mmol) were dissolved under nitrogen atmosphere in methanol (20 cm^3) to give a dark red solution, to which was added $PPN[AuBr_4]$ (105 mg, 0.1 mmol). A garnet solid precipitated which was collected by filtration, washed with methanol and dried *in vacuo*.

RESULTS AND DISCUSSION

The synthesis of complexes with dmit and analogues ligands with other calcogen atoms reported to date have been carried out starting from the COPh protected derivatives. In our case, the reaction of methanolic solutions of $dmise(COPh)_2$ in the presence of sodium to give Na_2dmise with chlorogold(I) complexes [AuClL] (L = phosphine or ylide) in 1 : 2 molar ratio, leads to dinuclear compounds where the dmise ligand acts as a bridge between the metallic centres, in a similar way to those reported by us for dmit derivatives [10] (See Scheme 1, i).

Complexes with the general formula $[Au_2(dmise)L_2]$ (L = PPh_3 **1**, $P(p\text{-}C_6H_4OMe)_3$ **2**, PPh_2Me **3**, PMe_3 **4**, CH_2PPh_3 **5**) can be isolated as air- and moisture-stable solids at room temperature. Their spectroscopic properties are in agreement with its formulation: one singlet in $^{31}P\{^1H\}$ NMR very close to the values observed in the analogues of dmit, since the selenoxo group is too far to affect these signals. Their IR spectra show a band at *ca* 950 cm^{-1} due to $\nu(C{=}Se)$ vibration [11] and a band at 580 cm^{-1} assignable to $\nu(Au{-}C_{ylide})$ [12]. The mass spectra (LSIMS+) show the parent peak M^+ at *m*/*z* (%): 1161 (15) **1**, 1341 (9) **2**, 1037 (15) **3**, 789 (20) **4**, with the expected isotopic distribution which in this case are illustrative because of the presence of six isotopes of selenium. As occurred for the dmit derivatives there



i) 2 [AuClL], ii) $[AuOClO_3PPh_2Me]$, iii) $[Au_2(\mu\text{-dppe})Cl_2]$, iv) $[Au_2(\mu\text{-dppm})Cl_2]$, v) [AuClL] + NBu_4Br, vi) 2 $PPN[Au(C_6F_5)Cl]$, vii) 1/2 $PPN[AuBr_4]$

Scheme 1.

are signals due to $[M+AuL]^+$ ion at m/z (%): 1620 (10) **1**, 1890 (6) **2**, 1434 (5) **3**, 1062 (30) **4**. The corresponding trinuclear complex in the case of L = PPh_2Me **6** can be achieved by a reaction of the dinuclear one **2** and a fresh solution of $[Au(OClO_3)(PPh_2Me)]$ (ii). Its ^1H NMR spectrum shows a doublet at 2.11 ppm $[^2J_{H\text{-}P} = 10.2$ Hz] and the $^{13}P\{^1H\}$ NMR at room temperature shows a broad signal, which is resolved in two singlets of relative intensity 2 : 1 at −60°C. This complex shows conductivity in acetone solution (5×10^{-4} M) characteristic of a 1 : 1 electrolyte [13] and the mass spectrum shows the parent ion at m/z (%) 1899 (16). According to the data for **1–6** complexes, we can postulate similar structures to those reported for dmit ligand, with the dmise ligand acting as μ_2 and μ_3 bridge.

Similar reaction with bisphosphine gold complexes (iii and iv) give different results depending on the phosphine. So, when dppe (1,2-bis(diphenylphosphine)ethane) is used, complex $[Au_2(dmise)(dppe)]$ **7** can be isolated, but with dppm (1,2-bis (diphenylphosphine) methane) $[Au_2(dmise)(dppm)]_2$ **8** is obtained instead. The $^{31}P\{^1H\}$ NMR for **7** consists on a singlet centred at 32.7 ppm in accordance with the proposed formulation and complex **8** shows an AA′XX′ system: $\delta_A = 37.7$ ppm, $\delta_X = 24.1$ ppm, $^2J_{AA'} = 81$ Hz, $^2J_{AX} = {}^2J_{A'X} = 46.4$ Hz. These data are very close to those reported to the dmit derivatives pointing out similar structures for dmit and dmise compounds [10,14] (see Scheme 1).

When the reaction i with [AuClL] is made in 1 : 1 molar ratio and after addition of NBu_4Br (v) anionic $NBu_4[Au(dmise)L]$ (L = PPh_3 **9**, PPh_2Me **10**) are obtained. Complexes **9** and **10** behave as 1 : 1 electrolytes in acetone solution in accordance with their formulation. Their $^{31}P\{^1H\}$ NMR spectra show singlets displaced down field with respect to the dinuclear compounds **1** and **3** (Table 1) and in a similar δ to those reported for the corresponding tricoordinated dmit complexes [10].

Other anionic gold dmise complexes can be obtained starting from anionic halo gold derivatives such as $PPN[Au(C_6F_5)Cl]$ and $PPN[AuBr_4]$ and reacting with a solution of Na_2dmise in 1 : 2 and 2 : 1 molar ratio, respectively (vi and vii). The corresponding complexes $(PPN)_2[Au_2(dmise)(C_6F_5)_2]$ **11** and $(PPN)[Au(dmise)_2]$ **12** are isolated as pink and garnet coloured solids and only **11** is soluble enough in acetone showing a Λ_M value characteristic of 2 : 1 electrolyte. The ^{19}F NMR spectrum of **11** shows three signals: −115.1 (m, F_o), −163.4 (t, F_p), −164.5 (m, F_m) in accordance with two equivalents C_6F_5 groups. Both complexes show in the mass spectra (LSIMS−) signals corresponding to the parent anion $[\mathbf{11}-2PPN]^-$, $[\mathbf{11}-PPN]^-$, $[\mathbf{12}-PPN]^-$ at m/z (%): 972 (10), 1510 (4) and 684 (8) respectively. It is noteworthy that the mass spectra of complex **11** shows other ion-molecule association as $[\mathbf{11}+Au(C_6F_5)-2PPN]^-$ and $[\mathbf{11}+Au(C_6F_5)-PPN]^-$ at m/z (%): 1336 (6) and 1874 (4).

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