# PREPARATION, PROPERTIES AND REACTIVITY OF GOLD COMPLEXES WITH SOME HETEROCYCLIC DITHIOCARBAMATES AS LIGANDS

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Abstract—The syntheses, properties and reactivity of the gold complexes AuRdtc,  $Au(Rdtc)_3$ ,  $Au(Rdtc)_2X$  and  $Au(Rdtc)X_2$  (X = Cl, Br; Rdtc = piperidine-, morpholine-, thiomorpholine-, piperazine-, N-methylpiperazine-, N-phenylpiperazine- and 4-phenylpiperidinedithiocarbamate) are reported. Elemental analysis, electrical conductance measurements, spectral (electronic and IR), magnetic susceptibility and thermogravimetric studies were used for characterization. The dithiocarbamato ligands exhibit both bidentate behaviour acting as S,S'-donors and monodentate behaviour acting as S-donors, depending on the type of the complex. The diamagnetic behaviour confirms the low-spin  $d^8$  configuration for Au(III) complexes and some metal–ligand and metal–halide stretches have been assigned.

As a part of our studies on the coordinating behaviour of the heterocyclic dithiocarbamate ligands towards transition metals, we report in this paper the synthesis, properties and reactivity of new complexes of gold(I) and gold(III) with the ligands indicated in Structure 1.



Structure 1.

We have previously described the complexes with d- and p-block metals, their reactivity towards nitrogen donor ligands, their mass spectral investigations and their structural characterization by XPS techniques.<sup>1-7</sup> It is of interest to monitor the influence of the different heterocyclic groups bearing different substituents in the ring, on the C···N and C···S bonds and, consequently, on the electron structure of the complexes. The nature of the heterocycle influences the behaviour of the dithiocarbamates through variation in the electron-releasing ability of the different amines.

# **RESULTS AND DISCUSSION**

The analytical data for the ligands and the complexes are reported in Tables 1 and 2, respectively. The complexes obtained were characterized by con-

$X = CH_2$	Pipdtc
= 0	Morphdtc
= S	Timdtc
= NH	Pzdtc
$= N - CH_3$	N – MePzdtc
$= N - C_6 H_5$	N-PhPzdtc
$= HC - C_6 H_5$	4 — PhPipdtc

ductivity measurements, magnetic moment studies, electronic, IR and far-IR spectra and thermal analyses (TG and DTG techniques). In Table 3 the most important IR bands with their assignments are listed. The electronic spectra data for the dithiocarbamato derivatives are collected in Table 4.

The compounds are stable at room temperature, insensitive to atmospheric oxygen and moisture, and are soluble in N,N'-dimethylformamide, pyridine, benzene, nitrobenzene and nitromethane. Conductance measurements in nitrobenzene and N,N'-dimethylformamide solution are indicative of 1:1 electrolytes for compounds of the Au(Rdtc)<sub>2</sub>X-

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	Found (required) %					
Compounds	С	Н	N	S		
$C_6H_{10}NS_2Na \cdot 2H_2O$ (PipdtcNa $\cdot 2H_2O$ )	33.0 (32.9)	6.5 (6.4)	6.4 (6.4)	29.1 (29.2)		
$C_5H_8NOS_2Na \cdot 2H_2O$ (MorphdtcNa $\cdot 2H_2O$ )	27.0 (27.1)	5.4 (5.5)	6.4 (6.3)	28.9 (29.0)		
$C_5H_8NS_3Na \cdot 2H_2O$ (TimdtcNa $\cdot 2H_2O$ )	25.1 (25.3)	5.1 (5.1)	5.9 (5.9)	40.6 (40.5)		
$C_5H_9N_2S_2Na \cdot 3H_2O$ (PzdtcNa $\cdot 3H_2O$ )	25.2 (25.2)	6.2 (6.3)	11.9 (11.8)	27.0 (26.9)		
$C_6H_{11}N_2S_2Na \cdot 2H_2O$ (N-MePzdtcNa $\cdot 2H_2O$ )	30.6 (30.7)	6.6 (6.5)	11.8 (11.9)	27.3 (27.4)		
$C_{11}H_{13}N_2S_2Na \cdot 2H_2O$ (N-PhPzdtcNa $\cdot 2H_2O$ )	44.7 (44.6)	5.6 (5.8)	9.5 (9.5)	21.5 (21.6)		
$C_{12}H_{14}NS_2Na \cdot 2H_2O$ (4-PhPipdtcNa $\cdot 2H_2O$ )	48.7 (48.8)	6.1 (6.1)	4.8 (4.7)	21.8 (21.7)		
$C_{12}H_{20}N_2S_4$ (Pip <sub>2</sub> tds)	44.9 (45.0)	6.3 (6.3)	8.7 (8.7)	40.2 (40.0)		
$C_{10}H_{16}N_2O_2S_4$ (Morph <sub>2</sub> tds)	37.0 (37.0)	5.0 (5.0)	8.7 (8.6)	39.7 (39.5)		
$C_{10}H_{16}N_{2}S_{6}$ (Tim <sub>2</sub> tds)	33.7 (33.7)	4.5 (4.5)	7.8 (7.8)	54.0 (53.9)		
$C_{10}H_{18}N_4S_4$ (Pz <sub>2</sub> tds)	37.3 (37.2)	5.4 (5.6)	17.5 (17.4)	39.8 (39.8)		
$C_{12}H_{22}N_4S_4$ (N-MePz <sub>2</sub> tds)	41.1 (41.1)	6.4 (6.3)	16.0 (16.0)	36.5 (36.6)		
$C_{22}H_{26}N_4S_4$ (N-PhPz <sub>2</sub> tds)	55.7 (55.7)	5.5 (5.5)	11.8 (11.8)	26.9 (27.0)		
$C_{24}H_{28}N_2S_4$ (4-PhPip <sub>2</sub> tds)	61.0 (61.0)	6.0 (6.0)	5.9 (5.9)	26.9 (27.1)		

Table 1. Analytical data for the dithiocarbamate sodium salts and for the thiuramdisulphides

type; all the remaining compounds were non-conducting in the above solvents, hence the absence of ionic species is indicative of the covalent nature of these complexes.<sup>8</sup>

# IR spectra

The IR spectra of the ligands and their gold complexes are given in Table 3. The thioureide band in the range 1440–1470 cm<sup>-1</sup> of the free ligands indicates considerable double-bond character of the carbon-nitrogen bond, this band being between the stretching frequencies of v(C=N) and v(C-N), which lie at 1690–1640 and 1350–1250 cm<sup>-1</sup>, respectively. This fact could be explained by taking into account that the electron-releasing ability of the heterocyclic group which, by forcing high electron density on the sulphur atom via the  $\pi$  system, produces greater double-bond character of the carbon-nitrogen bond whose stretching vibration, as a consequence, increases.

All complexes reported here show bands assigned to v(C - N) in the 1560-1480 cm<sup>-1</sup> range; in addition the 1:3 gold(III) derivatives show a second band between 1470-1445 cm<sup>-1</sup>; this fact clearly indicates that the dithiocarbamate groups are linked to the central metal ion in different ways. On passing from the dithiocarbamato sodium salts to the complexes, the  $v(C \rightarrow N)$  mode is shifted to higher energies and in particular undergoes blue shifts in the order Au(I) < Au(III). As regards the halo-derivatives, the  $v(C \rightarrow N)$  band is shifted to higher frequency following the order Au(Rdtc)X<sub>2</sub> > Au(Rdtc)<sub>2</sub>X. This sequence is due to the increase in electronegativity deriving from the increase of halide atoms in the complexes, and this fact promotes a higher positive charge on the nitrogen atom.

Taking into account the structure of the dithioanions which can be represented by the formalism shown in Scheme 1(a)-(d), we can conclude that the contribution from structure (d) is greater in the bishalo-derivatives and decreases on passing to the monohalo-derivatives and from gold(III) to gold(I).

The band in the region 1020–970 cm<sup>-1</sup> can be attributed to the prevailing contribution of  $v(C \rightarrow S)$ ; this value enables a decision to be made as to whether the dithio-ligand moiety is mono- or bidentate. The presence in the spectra of all the complexes (except the 1:3 gold derivatives), of only one strong band at about 1000 cm<sup>-1</sup> strongly supports bidentate coordination of the dithio-ligand, a doublet being expected in the 1000  $\pm$  70 cm<sup>-1</sup> range



Scheme 1.

Table 2. A	nalytical	data for	the gold	d complexes
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		Found (required) %			
Compounds	Colour	N	C	Н	S
Au(Pzdtc) <sub>3</sub>	Pale brown	12.3 (12.3)	26.2 (26.5)	3.6 (4.0)	28.2 (28.3)
Au(Pzdtc) <sub>2</sub> Cl	Brown	9.9 (10.1)	21.9 (21.6)	3.1 (3.3)	23.0 (23.1)
Au(Pzdtc)Cl <sub>2</sub>	Brown	6.5 (6.5)	13.9 (14.0)	2.1 (2.1)	14.8 (14.9)
$Au(Pzdtc)Br_2$	Brown	5.0 (5.4)	11.6 (11.6)	1.6 (1.8)	12.5 (12.4)
$Au(N-MePzdtc)_3$	Brown	11.6 (11.6)	30.0 (29.9)	4.6 (4.6)	26.6 (26.6)
Au(N-MePzdtc)Cl <sub>2</sub>	Red-brown	6.6 (6.3)	16.5 (16.3)	2.5 (2.5)	14.9 (14.5)
Au(N-MePzdtc)Br <sub>2</sub>	Ochre	5.3 (5.3)	13.7 (13.5)	2.1 (2.1)	12.3 (12.0)
Au(N-PhPzdtc) <sub>3</sub>	Hazel-brown	9.2 (9.2)	43.8 (43.6)	4.2 (4.3)	21.2 (21.2)
Au(N-PhPzdtc) <sub>2</sub> Cl	Pale brown	8.0 (7.9)	37.6 (37.4)	3.7 (3.7)	18.0 (18.1)
Au(N-PhPzdtc)Cl <sub>2</sub>	Pale brown	5.7 (5.5)	26.7 (26.2)	2.7 (2.6)	13.0 (12.7)
Au(N-PhPzdtc) <sub>2</sub> Br	Hazel-brown	7.2 (7.5)	35.0 (35.2)	3.5 (3.5)	17.0 (17.1)
Au(N-PhPzdtc)Br <sub>2</sub>	Hazel-brown	4.9 (4.7)	22.6 (22.2)	2.2 (2.2)	11.3 (10.8)
Au(Pipdtc) <sub>3</sub>	Dark violet	6.3 (6.2)	31.9 (31.9)	4.5 (4.5)	28.4 (28.4)
Au(Pipdtc) <sub>2</sub> Cl	Brown	5.1 (5.1)	26.1 (26.1)	3.6 (3.6)	22.8 (23.2)
Au(Pipdtc)Cl <sub>2</sub>	Light green	3.2 (3.3)	16.3 (16.8)	2.3 (2.3)	14.9 (15.0)
Au(Pipdtc) <sub>2</sub> Br	Brown	4.7 (4.7)	24.2 (24.1)	3.2 (3.4)	21.8 (21.5)
Au(Pipdtc)Br <sub>2</sub>	Yellow-ochre	2.7 (2.7)	13.6 (13.9)	1.7 (1.9)	12.4 (12.4)
Au(4-PhPipdtc) <sub>3</sub>	Pale green	4.8 (4.6)	47.6 (47.7)	4.6 (4.7)	21.3 (21.2)
Au(4-PhPipdtc) <sub>2</sub> Cl	Green	4.0 (4.0)	40.4 (40.9)	4.0 (4.0)	18.2 (18.2)
Au(4-PhPipdtc)Cl <sub>2</sub>	Pale yellow	2.8 (2.8)	28.5 (28.6)	2.8 (2.8)	12.8 (12.7)
Au(4-PhPipdtc) <sub>2</sub> Br	Yellow-green	3.8 (3.7)	37.7 (38.5)	3.6 (3.8)	17.0 (17.1)
Au(4-PhPipdtc)Br <sub>2</sub>	Orange	2.5 (2.4)	24.4 (24.3)	2.3 (2.4)	10.8 (10.8)
Au(Morphdtc) <sub>3</sub>	Brown	6.2 (6.1)	26.0 (26.3)	3.5 (3.5)	28.0 (28.1)
Au(Morphdtc) <sub>2</sub> Cl	Pale Brown	5.1 (5.0)	21.7 (21.6)	2.9 (2.9)	22.9 (23.0)
Au(Morphdtc)Cl <sub>2</sub>	Light green	3.3 (3.2)	14.1 (14.0)	1.9 (1.9)	15.7 (14.9)
Au(Morphdtc) <sub>2</sub> Br	Pale brown	4.7 (4.7)	20.4 (20.0)	2.7 (2.7)	21.4 (21.3)
Au(Morphdtc)Br <sub>2</sub>	Yellow-green	2.8 (2.7)	12.1 (11.6)	1.6 (1.6)	12.6 (12.4)
$Au(Timdtc)_3$	Brown	5.7 (5.7)	24.3 (24.6)	3.3 (3.3)	39.4 (39.4)
Au(Timdtc) <sub>2</sub> Cl	Pale brown	5.0 (4.8)	20.6 (20.4)	2.9 (2.7)	32.6 (32.7)
Au(Timdtc)Cl <sub>2</sub>	Light brown	3.0 (3.1)	13.2 (13.4)	1.8 (1.8)	21.5 (21.6)
Au(Timdtc) <sub>2</sub> Br	Pale brown	4.6 (4.4)	19.3 (19.0)	2.6 (2.5)	30.3 (30.4)
Au(Timdtc)Br <sub>2</sub>	Yellow	2.9 (2.6)	11.4 (11.2)	1.8 (1.5)	18.3 (18.0)
Au(Pzdtc)	Brown	7.5 (7.8)	16.8 (16.8)	2.5 (2.5)	17.8 (17.9)
Au(N-MePzdtc)	Grey-green	7.5 (7.5)	19.4 (19.4)	3.0 (3.0)	17.1 (17.2)
Au(N-PhPzdtc)	Grey-green	6.5 (6.4)	30.4 (30.4)	3.1 (3.0)	14.9 (14.8)
Au(Pipdtc)	Dark brown	3.9 (3.9)	20.1 (20.2)	2.9 (2.8)	18.0 (17.9)
Au(4-PhPipdtc)	Light green	3.3 (3.2)	33.2 (33.3)	3.2 (3.2)	14.8 (14.8)
Au(Morphdtc)	Pale yellow	4.0 (3.9)	17.0 (16.7)	2.2 (2.2)	17.7 (17.8)
Au(Timdtc)	Pale green	3.7 (3.7)	15.6 (16.0)	2.0 (2.1)	25.4 (25.6)

for monodentate behaviour.<sup>9-11</sup> On the contrary, a split band in the 1020–970 cm<sup>-1</sup> range for gold(III) tris-derivatives suggests that monodentate dithiocarbamato groups are present in the complexes. Further confirmation comes from an analysis of the position of the  $\nu$ (C···N) mode; in fact this band undergoes upward shifts for bidentate behaviour and it would undergo downward shifts or, at least, it would remain unchanged having the same value as for the free sodium dithiocarbamate in the case of monodentate coordination.<sup>12</sup>

Turning now to the 1:3 gold derivatives, from the behaviour of the  $v(C \rightarrow N)$  and  $v(C \rightarrow S)$  stretch-



some =C M ring deformation, as dem-

Table 3. Most important IR bands (cm<sup>-1</sup>) for the ligands and for the gold complexes

Compounds	v(C <u>···</u> N)	v(C <b></b> S)	$v(CS) + \delta(SCS)$	ν(M—S)	v(M—X)
PzdtcNa	1460vs	1000vs	560m		
N-McPzdtcNa	1450vs	995s	540m		
N-PhPzdtcNa	1465vs	975m	524m		
PipdtcNa	1465vs	965vs	525m		
4-PhPipdtcNa	1469vs	958ms	530m		
MorphdtcNa	1440vs	990s	535m		
TimdtcNa	1458vs	995s	490ms		
$Au(Pzdtc)_3$	1545vs, 1460ms	1020s, 990s	575m	425m, 400m	
Au(Pzdtc) <sub>2</sub> Cl	1530vs	1010m	570m	428m, 398m	
Au(Pzdtc)Cl <sub>2</sub>	1535vs	1005m	572m	420m, 395m	345m, 325m
Au(Pzdtc)Br <sub>2</sub>	1535vs	1000m	580m	422m, 385m	245m, 222m
Au(N-MePzdtc) <sub>3</sub>	1535vs, 1455ms	1000s, 970ms	535m	435m, 382m	
Au(N-MePzdtc)Cl <sub>2</sub>	1540vs	1000s	550m	410m, 372sh	348m, 325m
Au(N-MePzdtc)Br <sub>2</sub>	1555vs	995s	545m	402m, 370sh	249m, 224m
Au(N-PhPzdtc) <sub>3</sub>	1550vs, 1450ms	1010s, 995ms	530m	420m, 390m	
Au(N-PhPzdtc) <sub>2</sub> Cl	1545vs	1010s	525m	415m, 385sh	
Au(N-PhPzdtc)Cl <sub>2</sub>	1550vs	1015s	525m	440m, 395m	355m, 330m
Au(N-PhPzdtc) <sub>2</sub> Br	1545vs	1000s	515m	419m, 387sh	
Au(N-PhPzdtc)Br <sub>2</sub>	1550vs	1020s	520m	418m, 390m	246m, 238m
Au(Pipdtc) <sub>3</sub>	1550vs, 1460ms	1010s, 990s	515m	428m, 382m	
Au(Pipdtc) <sub>2</sub> Cl .	1530vs	1015s	520m	415m, 395sh	
Au(Pipdtc)Cl <sub>2</sub>	1550vs	995s	530m	410m, 390sh	356ms, 335m
Au(Pipdtc) <sub>2</sub> Br	1540vs	1005m	520m	420m, 393m	
Au(Pipdtc)Br <sub>2</sub>	1555vs	1010m	530m	417m, 392m	247m, 236m
Au(4-PhPipdtc) <sub>3</sub>	1540vs, 1470ms	1020m, 1000s	525m	415m, 385m	
Au(4-PhPipdtc) <sub>2</sub> Cl	1540vs	995m	525m	410m, 390m	
Au(4-PhPipdtc)Cl <sub>2</sub>	1550vs	995m	520m	415m, 385m	345m, 330m
Au(4-PhPipdtc) <sub>2</sub> Br	1545vs	990m	520m	418m, 390m	
Au(4-PhPipdtc)Br <sub>2</sub>	1550vs	995m	525m	416m, 386m	248m, 225m
Au(Morphdtc) <sub>3</sub>	1540vs, 1445ms	1020vs, 1000s	540m	430m, 398m	
Au(Morphdtc) <sub>2</sub> Cl	1530vs	1010s	540m	412m, 398sh	
Au(Morphdtc)Cl <sub>2</sub>	1540vs	1010s	535m	410m, 380sh	354m, 324m
Au(Morphdtc) <sub>2</sub> Br	1530vs	1000s	540m	409m, 388m	
Au(Morphdtc)Br <sub>2</sub>	1560vs	1000s	540m	408m, 388m	245m, 224m
Au(Timdtc) <sub>3</sub>	1535vs, 1455ms	990s, 975s	480m	409m, 393m	
Au(Timdtc) <sub>2</sub> Cl	1540vs	1000s	475m	410m, 392m	
Au(Timdtc)Cl <sub>2</sub>	1530vs	1010m	470m	408m, 394m	340m, 324m
Au(Timdtc) <sub>2</sub> Br	1535vs	1000s	470m	410m, 395m	
Au(Timdtc)Br <sub>2</sub>	1545vs	1000s	475m	410m, 392m	248m, 218m
Au(Pzdtc)	1530s	1010m	565m	419m, 395m	
Au(N-MePzdtc)	1480ms	990m	535m	430m, 378m	—
Au(N-PhPzdtc)	1540vs	1015m	520m	410m, 387m	
Au(Pipdtc)	1545vs	1000m	515m	408m, 380m	
Au(4-PhPipdtc)	1545vs	995m	530m	400m, 380m	—
Au(Morphdtc)	1525vs	990ms	540m	425m, 390m	—
Au(Timdtc)	1540vs	1000ms	490m	405m, 390m	******

onstrated by a detailed IR isotopic study on <sup>58</sup>Ni(II), <sup>62</sup>Ni(II), <sup>63</sup>Cu(II) and <sup>65</sup>Cu(II) dithio-complexes.<sup>2</sup>

The vibrational modes involving the heteroatom of the ring are unchanged relative to the free ligands, so any coordination to the metal via these oxygen, sulphur and nitrogen atoms is excluded. In the far-IR region, the bands of the ligands appear unchanged in the spectra of the complexes. New bands, absent in the spectra of the starting materials, are observed in the  $440-370 \text{ cm}^{-1}$  range and they can be assigned to the metal–sulphur stretching mode according to the normal coordinate analysis of the dithiocarbamato complexes and pre-

Table 4.	Main	absorption	bands i	in the	solid	state	electronic	spectra of	the
			C	omple	xes				

Compounds	$\max(\mathrm{cm}^{-1})$
Au(Pzdtc) <sub>3</sub>	36760, 32780, 31250, 23800, 17860
Au(Pzdtc) <sub>2</sub> Cl	36360, 29325, 24390, 19610, 17390
$Au(Pzdtc)Cl_2$	36290, 29200, 22180, 17750
$Au(Pzdtc)Br_2$	36360, 31240, 27770, 20000, 16660
$Au(N-MePzdtc)_3$	36360, 31250, 24390, 18180
Au(N-MePzdtc)Cl <sub>2</sub>	35100, 29850, 22220, 17860
Au(N-MePzdtc)Br <sub>2</sub>	35080, 30770, 22730, 17390
$Au(N-PhPzdtc)_3$	36800, 31150, 23810, 18200
Au(N-PhPzdtc) <sub>2</sub> Cl	37170, 32150, 22220, 17820
Au(N-PhPzdtc)Cl <sub>2</sub>	36750, 30670, 24090, 18350
Au(N-PhPzdtc) <sub>2</sub> Br	36360, 32260, 22990, 17820
$Au(N-PhPzdtc)Br_2$	36200, 30670, 24950, 17700
Au(Pipdtc) <sub>3</sub>	36360, 32150, 30770, 23530, 20000, 17090
Au(Pipdtc) <sub>2</sub> Cl	36100, 32050, 24390, 20410, 16000
Au(Pipdtc)Cl <sub>2</sub>	35710, 30770, 24100, 19230, 18000
Au(Pipdtc) <sub>2</sub> Br	36350, 32150, 24390, 21730, 17400
Au(Pipdtc)Br <sub>2</sub>	36230, 31050, 26660, 20000, 18000
Au(4-PhPipdtc) <sub>3</sub>	36350, 33900, 21740, 20000, 17900
Au(4-PhPipdtc) <sub>2</sub> Cl	35970, 32150, 22170, 18600
Au(4-PhPipdtc)Cl <sub>2</sub>	35850, 30770, 24390, 17390
Au(4-PhPipdtc) <sub>2</sub> Br	36360, 32000, 22220, 18180
Au(4-PhPipdtc)Br <sub>2</sub>	36000, 31270, 24240, 18000
Au(Morphdtc) <sub>3</sub>	37030, 30400, 23530, 17090
Au(Morphdtc) <sub>2</sub> Cl	37730, 31350, 29410, 23530, 19050, 16950
Au(Morphdtc)Cl <sub>2</sub>	36360, 34960, 29410, 24350, 18520
Au(Morphdtc) <sub>2</sub> Br	37300, 30770, 24450, 19700, 17100
Au(Morphdtc)Br <sub>2</sub>	37040, 31060, 24390, 19700, 16960
$Au(Timdtc)_3$	36760, 31350, 29850, 24450, 22220, 16660
Au(Timdtc) <sub>2</sub> Cl	36900, 30770, 24400, 20000, 17390
Au(Timdtc)Cl <sub>2</sub>	36490, 30300, 21500, 17390
Au(Timdtc) <sub>2</sub> Br	36360, 30860, 23810, 19050, 16390
Au(Timdtc)Br <sub>2</sub>	36350, 29850, 20400, 17240

vious work on gold derivatives.  $^{13,14}$  It is noteworthy that v(Au-S) increases in frequency as the oxidation number of the gold ion increases.

The bands present at 356–324 and at 249–218  $cm^{-1}$  in the chloro- and bromo-bishalo-derivatives, respectively, are attributed to the v(Au—Cl) and v(Au—Br) stretching frequencies for terminal halides.<sup>14,15</sup> The above mentioned metal-halide modes have not been found in the spectra of the Au(Rdtc)<sub>2</sub>X-type complexes, in agreement with the conductivity measurement results indicative of the 1:1 electrolyte character of these compounds.

#### Electronic spectra

The solid state electronic spectra of the complexes are reported in Table 4; these derivatives show absorptions in the 37730–26660 cm<sup>-1</sup> range, which can be attributed to intramolecular charge-transfer due to the chromophore group NCS<sub>2</sub>.<sup>16</sup> The band at higher energy is a  $\pi^* \leftarrow \pi$  transition located mainly in the N···C···S group.<sup>17,18</sup> The position of this band is sensitive to the number of the dithiocarbamato groups linked to the central atom showing the sequence

$$\operatorname{Au}(\operatorname{Rdtc})_3 > \operatorname{Au}(\operatorname{Rdtc})_2 X > \operatorname{Au}(\operatorname{Rdtc}) X_2.$$

The nature of the halogen has little influence on the position of this band and in general the sequence Cl > Br is observed. The second band at about 32000–29000 cm<sup>-1</sup> is attributed to a second  $\pi^* \leftarrow \pi$  transition of the S...C...S group.<sup>19</sup>

All the gold(III) complexes give a characteristic spectrum on the low energy side of the main charge-transfer edge. These transitions can be attributed to d-d bands, whose position is clearly indicative of a square-planar environment for the metal in these complexes. The most intense band between 24500–

22000 cm<sup>-1</sup> can be assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  band corresponding to the  $d_{xy} \rightarrow d_{xz}, d_{yz}$  transition, while the second weaker band, accompanied in some cases by a shoulder at lower energy, can be attributed to the first spin-allowed transition  ${}^{1}A_{1g} \rightarrow$  ${}^{1}A_{2g}$ .<sup>20</sup> All the complexes are diamagnetic according to the low-spin configuration of the metal ion.

# Thermogravimetric studies

Thermal analyses, performed using TG and DTG techniques, indicate that all the complexes undergo decomposition, transforming the dithiocarbamates into polysulphides and giving metallic gold as the end-product. The data give metal analyses in accord with the formulae given in Table 1.

# Reactivity

The gold(I) derivatives of the AuRdtc-type give, by reaction with the corresponding thiuramdisulphide, the gold(III) trisdithiocarbamates as final products; in this reaction Au(I) is oxidized to Au(III) according to the scheme:

$$AuRdtc + R_2tds \rightarrow Au(Rdtc)_3$$
.

Analogous to the above reported reaction, the dihaloaurate(I) ion is oxidized with thiuramdisulphide to obtain the complex  $Au(Rdtc)_2X$ :

$$AuX_2^- + R_2tds \rightarrow Au(Rdtc)_2X$$

The oxidative reaction of AuRdtc with halogens in methylene chloride produces the  $Au(Rdtc)X_2$  complexes:

$$AuRdtc + X_2 \rightarrow Au(Rdtc)X_2$$

The compounds of the Au(Rdtc)<sub>2</sub>X-type react with MAuX<sub>4</sub> (M = Na, K) in methylene chloride to give ionic complexes  $[AuX_4]^-[Au(Rdtc)_2]^+$  which easily rearrange, by boiling in methylene chloride, to the non-ionic isomers Au(Rdtc)X<sub>2</sub>. These last compounds, by reaction in methylene chloride with the dithiocarbamate sodium salts produce complexes of the type Au(Rdtc)<sub>2</sub>X :

 $Au(Rdtc)X_2 + RdtcNa \rightarrow Au(Rdtc)_2X + NaX.$ 

# **EXPERIMENTAL**

#### Preparation of the ligands

The sodium salts of the ligands were obtained by treating piperazine and 4-phenylpiperidine in dry diethylether and isopropyl alcohol; piperidine, morpholine, thiomorpholine, N-methylpiperazine and N-phenylpiperazine in dry diethylether with  $CS_2$  and adding NaOH with vigorous stirring over

4 h using molar ratios of amine:  $CS_2$ : NaOH = 1:1:1. The crude products were recrystallized from isopropyl alcohol.

The thiuramdisulphides have been prepared by treating an aqueous solution of the corresponding sodium dithiocarbamates with a slight excess of potassium esacyanoferrate(III),  $K_3$ [Fe(CN)<sub>6</sub>], at 0–5°C. The precipitates so formed were filtered, washed several times with cold water and dried over P<sub>4</sub>O<sub>10</sub>. The analytical data are summarized in Table 1.

# Preparation of the complexes

Commercial NaAuCl<sub>4</sub> and KAuBr<sub>4</sub> of high purity grade were used. The preparation of the 1:3 gold derivatives was performed in water, starting with NaAuCl<sub>4</sub> having a metal to ligand stoichiometrical ratio of 1:3 or by the reaction of the gold(I) dithiocarbamates with the corresponding thiuramdisulphides in a 1:1 stoichiometrical ratio.

The gold(I) complexes were prepared by starting with MAuX<sub>4</sub> (X = Cl, Br) in aqueous solution cooled to 0°C, carefully reducing these with a water solution of Na<sub>2</sub>SO<sub>3</sub> (0.1 M) until the solution became colourless and then treating with an aqueous solution of the ligands in a 1:1 molar ratio.

The gold(III) chloro- and bromo-derivatives were obtained by metathetical reactions starting with a water solution of  $MAuX_4$  and the dithiocarbamate sodium salts in 1:1 or 1:2 metal to ligand molar ratios in the same solvent.

The Au(Rdtc)<sub>2</sub>X-type complexes can be obtained by treating a gold(I) solution, prepared according to the method described above, with thiuramdisulphides dissolved in methanol, in a 1:1 molar ratio. A second way consists of reaction of the compounds Au(Rdtc)X<sub>2</sub> in methylene chloride with the dithiocarbamato sodium salts dissolved in methanol.

Compounds of the Au(Rdtc)X<sub>2</sub>-type can be obtained starting with Au(Rdtc)<sub>2</sub>X and MAuX<sub>4</sub>, (M = Na, K; X = Cl, Br) and refluxing in methylene chloride under stirring, or by oxidative reaction of the AuRdtc derivatives with halogens in methylene chloride at room temperature.

All the precipitates were filtered, washed with ethanol, diethylether and dried over  $P_4O_{10}$ .

# Electronic spectra

The electronic spectra were recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 5000–45000 cm<sup>-1</sup> region. Samples were prepared by grinding the complexes on a filter paper as a support.

#### IR spectra

The IR spectra have been recorded in the 4000– 50 cm<sup>-1</sup> range with a Perkin–Elmer 180 spectrophotometer at the "Centro Interdipartimentale Grandi Strumenti" of Modena University. The spectra in the 4000–400 cm<sup>-1</sup> range were measured for KBr discs or Nujol mulls. Far-IR spectra were measured on Nujol mulls suported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

#### Magnetic susceptibility measurements

These measurements were carried out by Gouy's method at room temperature. The molecular susceptibilities were corrected for the diamagnetism of the component atoms by the use of Pascal's constants. All the complexes were diamagnetic.

#### Conductivity measurements

These measurements were carried out with a WTW LBR type conductivity bridge for freshly prepared  $10^{-3}$  M solutions in DMF at  $25\pm0.1^{\circ}$ C.

#### Thermal analyses

Thermogravimetric analyses (TG and DTG) were performed in air on a Mettler TG50 thermobalance equipped with a Mettler TC10TA processor. A scan rate of  $10^{\circ}$ C min<sup>-1</sup> was used.

## Analyses

Carbon, nitrogen, hydrogen and sulphur were determined with a Carlo Erba 1106 elemental analyser.

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