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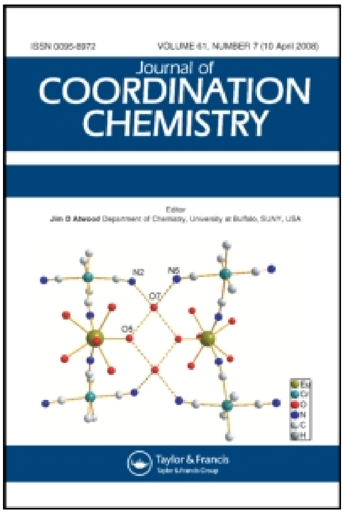

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SILVER AND GOLD COMPLEXES WITH CYCLIC CARBODITHIOATES AS LIGANDS

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SILVER AND GOLD COMPLEXES WITH CYCLIC CARBODITHIOATES AS LIGANDS

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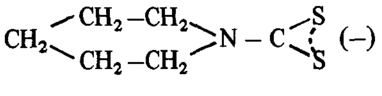
The preparation and magnetic susceptibility, electronic, infrared, electrical conductivity and thermogravimetric studies of a series of monomethylsubstituted piperidine dithiocarbamates of silver(I), gold(I) and gold(III) are reported. The complexes are formulated as AgRdtc, AuRdtc, $Au(Rdtc)_3$, $Au(Rdtc)_2X$ and $AuRdtcX_2$ ($X = Cl, Br$). The dithioligands 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 of the gold(III) derivatives is in accord with the usual low-spin d^8 configuration. The metal-sulphur and metal-halide stretches have also been assigned and are in accord with the proposed structures. The molecular weight determinations indicate monomeric structures for the $Au(Rdtc)_3$ and $AuRdtcX_2$ complexes and dimeric structures for the $Au(Rdtc)_2X$ derivatives. The results of the spectroscopic studies indicate that in the $Au(Rdtc)_3$ complexes one of the dithiocarbamate groups must act as a bidentate ligand, while the other two act as monodentates giving square planar structures.

Keywords: Silver; Gold; Dithiocarbamates; synthesis; complexes

INTRODUCTION

In previous papers we have reported the synthesis and characterization of many d- and p-block metal complexes with monomethylsubstituted piperidine dithiocarbamates in order to study the different behaviour of the ligands in which dialkly groups are replaced by heterocycles and in which, furthermore, the heterocycle bears different substituents or the same substituent in different positions.[1–4] The spectrochemical properties of these ligands are of particular interest, as regards the influence of the different heterocyclic groups on the C⩵N and C⩵S bonds and, consequently, on the electronic structure of the complexes.



This paper deals with the preparation and characterization of trisdithiocarbamate complexes of gold(III), $Au(Rdtc)_3$, monodithiocarbamates of gold(I) and silver(I), MRdtc, and with a new series of monohalobisdithiocarbamates, $Au(Rdtc)_2X$, and bishalomonodithiocarbamates, $AuRdtcX_2$, where $X = Cl$, Br, and $Rdtc^-$ are the three derivatives of piperidine dithiocarbamate 2-, 3-, and 4-methylpiperidine dithiocarbamate, hereafter abbreviated as 2-MePipdtc, 3-MePipdtc, and 4-MePipdtc, respectively.

RESULTS AND DISCUSSION

The complexes obtained together with their analytical data are reported in Table I. In Table II are listed the most important infrared bands with their assignments. The electronic spectral data for the dithiocarbamate derivatives are collected in Table3. The compounds are stable at room temperature, insensitive to atmospheric oxygen and moisture, and are soluble in benzene, nitrobenzene, pyridine, *N,N*-dimethylformamide (DMF) and nitromethane. Conductance measurements in nitrobenzene and in DMF solution indicate the absence of ionic species and hence the covalent nature of the compounds.

Infrared spectra

The most important i.r. peaks for the free ligands as sodium salts and the complexes are reported in Table II; the spectra of the complexes show the vibrational modes due to the methyl group at the same frequencies as in the free ligands.[5] The thioureide band between 1407 and 1424 cm^{-1} in the free ligands indicates considerable double-bond character in the $\mathrm{C}\overset{..}{-}\mathrm{N}$ bond, the band appearing between the stretching frequencies of $\nu(\mathrm{C{=}N})$ (1640–1690 cm^{-1}) and $\nu(\mathrm{C{-}N})$ (1250–1350 cm^{-1}). This fact may be attributed to the electron releasing ability of the heterocyclic group which forces high electron density towards the sulphur atoms, *via* the π system, producing as a consequence greater double bond character in the carbon-nitrogen bond and shifting $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$ to higher energy.

All the dithiocarbamate derivatives presented here show a band, assigned to $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$, in the 1412–1557 cm^{-1} range; in addition the 1:3 gold(III) complexes show a second band between 1413 and 1426 cm^{-1} and this fact clearly indicates that the Rdtc^{-} groups are linked to the central metal ion in different ways. The $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$ mode is shifted to higher energies in the sequence Au(I) < Ag(I) < Au(III).

In the haloderivatives of gold(III), the $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$ band is shifted to higher frequency

TABLE I
Analytical data for the complexes

Compound	Colour	Found (Required) %			
		N	C	H	S
Ag(2-MePipdtc)	dark yellow	4.9(5.0)	29.6(29.8)	4.4(4.3)	22.6(22.7)
Ag(3-MePiipdtc)	yellow	5.0(5.0)	29.4(29.8)	4.2(4.3)	22.5(22.7)
Ag(4-MePipdtc)	white	5.0(5.0)	29.8(29.8)	4.3(4.3)	22.5(22.7)
Au(2-MePipdtc)	dark yellow	4.0(3.8)	22.6(22.7)	3.5(3.3)	17.2(17.3)
Au(3-MePipdtc)	yellow	3.8(3.8)	22.4(22.7)	3.3(3.3)	17.6(17.3)
Au(4-MePipdtc)	dark yellow	3.9(3.8)	22.9(22.7)	3.4(3.3)	17.2(17.3)
Au(2-MePipdtc)$_3$	brown	5.8(5.8)	34.6(35.0)	5.1(5.0)	26.3(26.7)
Au(3-MePipdtc)$_3$	brown	5.8(5.8)	34.9(35.0)	4.9(50)	26.8(26.7)
Au(4-MePipdtc)$_3$	dark brown	5.8(5.8)	34.8(35.0)	5.0(5.0)	26.1(26.7)
Au(2-MePipdtc)$_2$Cl	brown	4.8(4.8)	28.9(28.9)	4.2(4.2)	22.1(22.1)
Au(2-MePipdtc)$_2$Br	brown	4.5(4.5)	27.0(26.9)	4.1(3.9)	20.3(20.5)
Au(3-MePipdtc)$_2$Cl	brown	4.8(4.8)	28.8(28.9)	4.0(4.2)	22.2(22.1)
Au(3-MePipdtc)$_2$Br	brown	4.5(4.5)	27.0(26.9)	3.9(3.9)	20.4(20.5)
Au(4-MePipdtc)$_2$Cl	brown	4.8(4.8)	28.9(28.9)	4.3(4.2)	22.4(22.1)
Au(4-MePipdtc)$_2$Br	brown	4.4(4.5)	26.6(26.9)	3.7(3.9)	20.2(20.5)
Au(2-MePipdtc)Cl$_2$	ochre	3.2(3.2)	19.5(19.0)	2.8(2.7)	14.9(14.5)
Au(2-MePipdtc)Br$_2$	light brown	2.6(2.6)	15.9(15.8)	2.1(2.3)	12.2(12.1)
Au(3-MePipdtc)Cl$_2$	ochre	3.2(3.2)	19.5(19.0)	2.6(2.7)	14.6(14.5)
Au(3-MePipdtc)Br$_2$	ochre	2.6(2.6)	16.2(15.8)	2.1(2.3)	12.3(12.1)
Au(4-MePipdtc)Cl$_2$	ochre	3.2(3.2)	19.7(19.0)	2.6(2.7)	14.2(14.5)
Au(4-MePipdtc)Br$_2$	dark yellow	2.7(2.6)	16.0(15.8)	2.2(2.3)	11.6(12.1)

TABLE II
Most important infrared bands (cm^{-1}) for the complexes and ligands.[a]

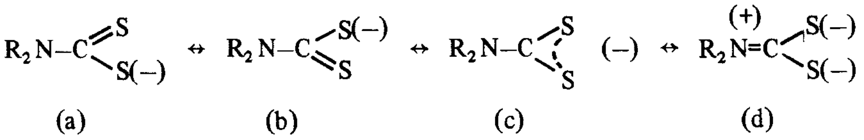
Compounds	$\nu(C\doteq N)$	$\nu(C\doteq S)$	$\nu(CS)+$ $\delta(SCS)$	$\nu(M\text{-}S)$	$\nu(M\text{-}X)$
Ag(2-MePipdtc)	1421vs	931s	533m	401m	—
Ag(3-MePipdtc)	1427vs	940s	551m	400m	—
Ag(4-MePipdtc)	1431vs	940s	522m	401mw	—
Au(2-MePipdtc)	1412vs	944s	534m	414sh, 404m	—
Au(3-MePipdtc)	1428vs	950ms	551m	411m, 391m	—
Au(4-MePipdtc)	1429vs	949s	528m	411m, 401m	—
Au(2-MePipdtc)$_3$	1518vs, 1413vs	957sh, 931s	536m	437m, 421m	—
Au(3-MePipdtc)$_3$	1533vs, 1421vs	979sh, 950s	554m	421ms, 415m	—
Au(4-MePipdtc)$_3$	1545vs, 1426vs	968s, 955sh	529m	431m, 413m	—
Au(2-MePipdtc)$_2$Cl	1529vs	932ms	530m	425m, 419m	—
Au(3-MePipdtc)$_2$Cl	1548vs	938m	553m	422m, 414m	—
Au(4-MePipdtc)$_2$Cl	1555vs	941ms	521m	411sh, 402s	—
Au(2-MePipdtc)$_2$Br	1525vs	931ms	533m	420sh, 411m	—
Au(3-MePipdtc)$_2$Br	1543vs	951s	549m	421sh, 414m	—
Au(4-MePipdtc)$_2$Br	1553vs	955s	524m	413m, 404m	—
Au(2-MePipdtc)Cl$_2$	1535vs	940m	533m	432m, 413vs	357s, 336m
Au(3-MePipdtc)Cl$_2$	1555vs	950m	548m	426mw, 413s	357s, 333m
Au(4-MePipdtc)Cl$_2$	1557vs	953s	544m	423m, 404vs	356s, 335m
Au(2-MePipdtc)Br$_2$	1533vs	945m	533m	427m, 412s	249ms, 235m
Au(3-MePipdtc)Br$_2$	1550vs	948m	544m	423m, 413s	250s, 235m
Au(4-MePipdtc)Br$_2$	1556vs	953m	534m	419m, 405s	250s, 239m

[a] 2-MePipdtcNa: $\nu(C\doteq N)$ 1407vs; $\nu(C\doteq S)$ 943s; $\nu(CS)+\delta(SCS)$ 532ms. 3-MePipdtcNa: $\nu(C\doteq N)$ 1418vs; $\nu(C\doteq S)$ 951s; $\nu(CS)+\delta(SCS)$ 530 ms. 4-MePipdtcNa: $\nu(C\doteq N)$ 1424vs; $\nu(C\doteq S)$ 950s; $\nu(CS)+\delta(SCS)$ 522ms.

TABLE III
Main absorption bands in the solid state electronic spectra of the complexes (cm^{-1}).

Compound	$\lambda_{max}(cm^{-1})$
Ag(2-MePipdtc)	42550, 34960, 32250, 27770
Ag(3-MePipdtc)	41660, 34130, 32260, 27030
Ag(4-MePipdtc)	41660, 34840, 32150, 27170
Au(2-MePipdtc)	43480, 37735sh, 35335, 32155, 29585
Au(3-MePipdtc)	43055, 35715, 31545, 29500
Au(4-MePipdtc)	38315sh, 35460, 31445, 28985
Au(2-MePipdtc)$_3$	43860, 35970, 32050, 29500, 23695, 20835sh, 16665sh
Au(3-MePipdtc)$_3$	43105, 35970, 31250, 29410, 23220, 16665sh
Au(4-MePipdtc)$_3$	36100, 32260, 29325, 23925, 20000sh, 16395sh
Au(2-MePipdtc)$_2$Cl	35710, 31250, 26955, 24390, 16670sh
Au(3-MePipdtc)$_2$Cl	35710, 31250, 26880, 24380, 21645sh, 16670sh
Au(4-MePipdtc)$_2$Cl	35710, 31250, 27100, 24390, 16950sh
Au(2-MePipdtc)$_2$Br	35710, 31250, 27190, 24390, 16670sh
Au(3-MePipdtc)$_2$Br	35710, 31250, 26800, 24350, 21645sh, 17240sh
Au(4-MePipdtc)$_2$Br	35710, 31545, 27030, 22220
Au(2-MePipdtc)Cl$_2$	37040sh, 35590, 30030, 26950, 24390
Au(3-MePipdtc)Cl$_2$	37040sh, 35340, 29940, 27625, 24390
Au(4-MePipdtc)Cl$_2$	37040sh, 35590, 30120, 27550, 24380
Au(2-MePipdtc)Br$_2$	37040sh, 34130, 29850, 26810, 24690, 20835sh, 16670sh
Au(3-MePipdtc)Br$_2$	37040sh, 34485, 29850, 26820, 24690, 20835sh, 16670sh
Au(4-MePipdtc)Br$_2$	37455sh, 34845, 31250, 26660, 24690, 20835sh, 16660sh

than in the trisderivatives following the order $AuRdtcCl_2 > AuRdtcBr_2 > Au(Rdtc)_2Cl > Au(Rdtc)_2Br$. The increase in this sequence is apparently due to the increasing electronegativity of the halogen, resulting in a higher positive charge on the nitrogen atom. In fact the bishaloderivatives have $\nu(C \mathrel{\overset{\cdots}{-}} N)$ modes at higher values than the monohalocomplexes. Taking into account the structure of the dithioligands, represented by the formalism shown in (a) to (d) we suggest that the contribution of the structure (d) is greatest in the haloderivatives and decreases on passing from gold(III) to silver(I) and gold(I). As regards the methyl group in the piperidine ring, the carbon-nitrogen vibration increases in frequency in the sequence 2-MePipdtc < 3-MePipdtc < 4-MePipdtc.



The $\nu(C \mathrel{\overset{\cdots}{-}} S)$ value enables a decision to be made as to whether the dithioligand 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 in the 931–955 cm^{-1} region strongly supports bidentate coordination of the dithioligand, a doublet being expected in the 1000 ± 70 cm^{-1} range for monodentate behaviour.[5–7] On the contrary, a split band in the 931–979 cm^{-1} range for the gold(III) trisderivatives suggests that monodentate dithiocarbamato groups are present in the complexes. Further confirmation comes from an analysis of the position of the $\nu(C \mathrel{\overset{\cdots}{-}} N)$ mode; in fact this band undergoes blue shifts for bidentate behaviour and it would be shifted to lower wavenumber or remain unchanged at about the same value of the free dithiocarbamato sodium salt in the case of monodentate coordination.[8]

Turning now to the 1:3 gold(III) derivatives, from the behaviour of the $\nu(C \mathrel{\overset{\cdots}{-}} N)$ and $\nu(C \mathrel{\overset{\cdots}{-}} S)$ modes, we propose the simultaneous presence of bidentate and monodentate $Rdtc^-$ groups in monomeric complexes as suggested by the molecular weight determinations mentioned below. In all the other complexes the presence of only one $\nu(C \mathrel{\overset{\cdots}{-}} S)$ band and the shift of the $\nu(C \mathrel{\overset{\cdots}{-}} N)$ mode point to bidentate behaviour of the ligands. The vibrational modes present in the 521–554 cm^{-1} range can be ascribed to the contribution of $\nu(CS)+\delta(SCS)$ and of $M{<}\genfrac{}{}{0pt}{}{S}{S}{>}C =$ ring deformation as previously shown by a detailed infrared isotopic study on nickel(II) and copper(II) dithiocomplexes.[9]

In the far infrared region, the bands of the ligands are unchanged in the spectra of the complexes. New bands, absent in the spectra of the starting materials, are observed in the 391–437 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 to previous works on gold derivatives.[10,11] It is noteworthy that $\nu(Au\text{–}S)$ lies at higher energies in the gold(III) than in the gold(I) derivatives because of the higher oxidation state of the metal; this gold(III)-sulphur mode undergoes downward shifts on passing to the halocomplexes in the sequence $AuRdtcCl_2 > AuRdtcBr_2 > Au(Rdtc)_2Cl > Au(Rdtc)_2Br$ as a consequence of the decreasing electronegativity of the ligands. Furthermore, $\nu(Au\text{–}S)$ in the haloderivatives is shifted to lower energies in the trend 2-MePipdtc > 3-MePipdtc > 4-MePipdtc.

The bands present at 333–357 cm^{-1} and at 235–250 cm^{-1}, but only in the bishaloderivatives (chloro- and bromo- respectively), are attributed to the gold-chlorine and gold-bromine stretching frequencies for terminal halides.[11,12] The above mentioned metal-halide modes have not been found in the spectra of the $Au(Rdtc)_2X$ complexes, whereas a new band is present at about 180 cm^{-1} in the bromo-derivatives only, which can be tentatively assigned to ν(Au-Br) for bridging bromine atoms. The assignment of the similar ν(Au-Cl) mode for bridging chlorine atoms is made difficult by the presence of ligand bands in the expected region. We propose dimeric structures for the $Au(Rdtc)_2X$ derivatives in agreement with conductivity measurements and molecular weight determinations.

Electronic spectra

The solid state electronic spectra of the complexes are given in Table III. The complexes show absorptions in the 43860-26660 cm^{-1} region, which can be attributed to intramolecular charge transfer. In particular, those between 36100 and 34130 cm^{-1} can be ascribed to the NCS_2 chromophore.[13] The band at higher energy, in some cases accompanied by a shoulder, is a $\pi \rightarrow \pi^*$ transition located mainly in the CS_2 group.[14,15] The position of this band is sensitive to the nature of the central atom and to its oxidation state, showing the characteristic order Au(III) > Au(I) > Ag(I). Passing to the gold(III) haloderivatives the sequence $Au(Rdtc)_2X$ > $AuRdtcX_2$ is observed. The second band in the 32260-29850 cm^{-1} range is attributed to a second $\pi — \pi^*$ transition of the $S\overset{...}{-}C\overset{...}{-}S$ group.[16] The band at 29585-26660 cm^{-1} may be assigned to a $n \rightarrow \pi^*$ transition located on the sulphur atoms.[17,18]

All the gold(III) complexes give a characteristic spectrum on the low energy side of the main charge transfer band edge. The position of the d-d bands is clearly indicative of a square planar environment for the metal in the complexes. The most intense component at about 23000-24000 cm^{-1} could be assigned to the $^1A_{1g} \rightarrow {}^1E_g$ band corresponding to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition, while the second weak band, present only as a shoulder and absent in some derivatives, can be attributed to the first spin-allowed transition $^1A_{1g} \rightarrow {}^1A_{2g}$.[19]

The molecular weight determinations carried out on the gold(III) derivatives show that the trisderivatives are monomeric in nitrobenzene solution, thus confirming the conclusions reached from the infrared studies. As for the haloderivatives, the $AuRdtcX_2$ complexes are monomeric and the $Au(Rdtc)_2X$ derivatives are dimeric, in good accord with the results of the conductivity measurements. Thermogravimetric studies indicate that all the complexes leave a metal residue passing through polysulphides in the 35-1000°C temperature range. The data give metal analyses in accord with the formulae given in Table I.

EXPERIMENTAL

Preparation of the ligands

The sodium salts of the ligands were prepared by reaction of 2-methyl-, 3-methyl-, or 4-methylpiperidine (reagent grade) in dry ethyl ether with CS_2 and NaOH with vigorous stirring over a 5h. period. Molar ratios used were amine:CS_2:NaOH=1:1:1. The crude products were recrystallized from isopropyl alcohol.

Analyses: Calcd. for $C_7H_{12}NS_2Na \cdot 2.5H_2O$: C 34.7; H 7.1; N 5.8; S 26.5%. Found for 2-MePipdtcNa$\cdot 2.5H_2O$: C 34.4; H 7.0; N 5.8; S 26.2%; 3-MePipdtcNa$\cdot 2.5H_2O$: C 34.1; H 7.1; N 5.7; S 26.0%; 4-MePipdtcNa$\cdot 2.5H_2O$: C 34.9; H 7.0; N 5.9; S 26.3%.

Preparation of the complexes

Commercial $NaAuCl_4$, $KAuBr_4$ and $AgNO_3$ of high purity were used. The preparation of the 1:3 gold derivatives and of the silver complexes was peformed in water starting with $NaAuCl_4$ and $AgNO_3$ in 1:3 and 1:1 metal to ligand stoichiometrical ratios, respectively. The gold(I) complexes were prepared starting with $MAuX_4$ (X = Cl, Br) in aqueous solution cooled at 0°, carefully reduced with a solution of Na_2SO_3 and then treated 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 precipitates were filtered, washed with ethanol and ether and dried over P_4O_{10}.

Physical measurements

The i.r. spectra were recorded in the 4000–50 cm^{-1} region with a Perkin-Elmer 180 spectrophotometer at the Instruments Centre of Modena University. The spectra in the 4000–400 cm^{-1} region were measured as KBr discs or Nujol mulls. Far-i.r. spectra were measured in Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen. The electronic spectra have been recorded with a Shimadzu MPS-50L spectrophotometer in the solid state in the 5000–45000 cm^{-1} range, the method of Venanzi and coworkers being used.[20] The molecular weights were determined in nitrobenzene by the cryoscopic method. Thermogravimetric analyses were performed in air on a Mettler TG50 thermobalance equipped with a Mettler TC10TA processor. Conductivity measurements were carried out with a WTW LBR conductivity bridge using freshly prepared 10^{-3} M solutions in DMF and nitrobenzene at 25 ± 0.1°. Carbon, nitrogen, hydrogen and sulphur were determined using a Carlo Erba 1106 elemental analyzer.

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