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Gold(III) Complexes of Dithiomalonamides

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Dithiomalonamides are structurally analogous to β-dithioketones, with the advantage of being isolable ligands which can be comparatively studied with their complexes. In previous papers we studied the nickel (II)[1,2] and palladium(II)[3,4] dithiomalonamides and found that they act as chelating agents, forming ML_2 complexes, in which the replacement of a proton by a metal cation produces six-membered rings with the two donor sulfur atoms, and as coordinating agents through nitrogen and sulfur, forming six-membered ring complexes of the type ML_2X_2 and $PdLX_2$.

In this note we report the preparation and study of gold complexes of dithiomalonamide (hdtma), N,N′-dimethyl-dithiomalonamide (hdmma) and N,N′-diphenyl-dithiomalonamide (hdpma).

The prepared compounds have the composition AuL_2Cl (L = dtma, dpma) and $AudmmaCl_2$ and were investigated by means of magnetic susceptibility measurements, electronic and infrared spectra, electric conductivity and polarographic measurements.

The complexes have a stoichiometry appropriate for monovalent and divalent gold, respectively; however, this does not imply the actual presence of Au(II), which is only known in complexes with maleonitriledithiolate[5] and phthalocyanine[6]. The remarkable analogies of the i.r. (Table I) and electronic (Table II) spectra of our complexes with those of ML_2 (M = Ni, Pd; L = dtma, dmma, dpma) complexes[1-4], for which an S_4-coordination and the chelating behaviour of the ligands is well established, together with their diamagnetism, suggest that our Au complexes are isomorphous and probably isostructural with ML_2 complexes, and have a square-planar low-spin d^8 configuration, Au(III) being present. The assignments of the electronic spectra (Table II) are made on this basis. A spectrochemical order for the d^8 metals of the type Au > Pd > Ni is found from the first *d–d* band.

The conductivities of the AuL_2Cl complexes in dimethylformamide (DMF) solution (λ_M = 45 and 32 ohm^{-1} cm^2 mol^{-1} for $Au(dtma)_2Cl$ and $Au(dpma)_2Cl$, respectively) may indicate the presence of 1:1 electrolytes, the low conductivity values being due to an interaction of the type "outer-sphere association" of the chloride anion with the cationic complex, as found for other chloro-complexes[7].

The polarographic results for the AuL_2Cl complexes confirm the presence of trivalent gold. No polarographic reduction of the free ligands was observed in DMF solution from 0 to –1.1 V. The reduction of the complexes occurs with one three-electron wave, the total number of electrons added ($n \cong 2.7$ and 3.2 for $Au(dtma)_2Cl$ and $Au(dpma)_2Cl$ respectively) resulting from the Ilkovič equation[8]. The reduction potential found was $E_{1/2} = -0.48$ V for $Au(dtma)_2Cl$ and $E_{1/2} = -0.51$ V for $Au(dpma)_2Cl$. From the analysis of the polarographic curves, recorded with different drop-times and concentrations, the process seems to be diffusion controlled only for fast drop-times and very low concentrations, and to be irreversible under these conditions.

Since there is also a striking resemblance between the far i.r. spectra of ML_2 complexes and AuL_2Cl complexes (L = dtma, dpma), a structure containing Au–Cl bonds may be excluded, while in the $AuLCl_2$ complex the presence of three bands at 363vs, 178m and 140s, absent in the spectra of $M(dmma)_2$[2,4] complexes, may suggest the presence of the $AuCl_4^-$ group[9,10].

TABLE I. Characteristic I.R. Bands of the Au Complexes.

	$Au(dtma)_2Cl$	$Au(dmma)Cl_2$[a]	$Au(dpma)_2Cl$
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	1520vsb	1532vs	1495vs
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ + $\delta(\mathrm{C-H})$		1428m	1425w
$\delta(\mathrm{C-H})$ + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	1350vs	1347m	1316m
$\nu(\mathrm{C\cdots C})$	1273ms	1257s	1252vs
$\pi(\mathrm{C-H})$	801m	777ms	804s
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	642m	629ms	632s
$\nu(\mathrm{M-S})$	374m	396m	
	305m	330sh	328wb

[a] This complex shows in the far i.r. spectra three new bands at 363vs, 178m, 140s assignable to Au–Cl modes (see text).

TABLE II. Electronic Spectra of the Complexes in Methylcellosolve.

Transition	$Au(dtma)_2Cl$	$Au(dmma)_2AuCl_4$	$Au(dpma)_2Cl$
${}^1A_g \rightarrow {}^1B_{1g}$ $(x^2 - y^2 \rightarrow xy)$	22470sh (2.87)	21740sh (2.64)	21050sh (3.48)
M → L charge transfer			
${}^1A_g \rightarrow {}^1B_{3u}$ $(yz \rightarrow L(\pi^*))$	26320sh (4.04)		26530sh (4.26)
L → M charge transfer			
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ $(L(\pi) \rightarrow xy)$	34130 (4.54)	33330 (4.60)	
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ $(L(\sigma) \rightarrow xy)$	47170 (4.02)	44840 (4.42)	41320sh (4.48)
$L \rightarrow L^*$			
${}^1A_g \rightarrow {}^1B_{2u}$	28990 (4.06)	29940 (4.23)	30490 (4.74)
${}^1A_g \rightarrow {}^1B_{1u}$	37880 (4.59)	37310 (4.57)	

All the experimental results agree with the ionic configuration of all the complexes of the type $AuL_2^+X^-$(L = dtma, dpma and X = Cl; L = dmma and X = $AuCl_4^-$).

The conductivity value of ~ 66 ohm^{-1} cm^2 mol^{-1} in DMF solution of $Au(dmma)_2AuCl_4$ complex confirms the ionic nature of the complex. Owing to the instability of its DMF solution the polarographic reduction was not recorded.

The bands found at 374 - 396 and 305 - 330 cm^{-1} in the far i.r. spectra of the complexes (Table I) are assigned to the gold–sulfur stretching modes in agreement with the values found for the ML_2 complexes (Table I) and with the other values given in literature for the Au(III)–S bond[11,12].

Experimental

The ligands were prepared as previously described[1,2].

The complexes were prepared by adding to an ethanolic solution (15 ml) of the ligand (5 × 10^{-4} mM) an aqueous solution (3 ml) of the metal salt ($HAuCl_4 \cdot 3H_2O$) (5 × 10^{-4} mM). The compound precipitated instantaneously and was washed with ethanol and ethyl ether and dried *in vacuo* at room temperature.

Au(dtma)₂Cl: Anal. $C_6H_{10}N_4S_4ClAu$. Calcd.: Au 39.33, C 14.38, H 2.41, Cl 7.07. Found: Au 39.87, C 14.65, H 2.78, Cl 6.09. Yield% = 70.

AudmmaCl₂: Anal. $C_5H_9N_2S_2Cl_2Au$. Calcd.: Au 45.81, C 13.95, H 2.33, Cl 16.49. Found: Au 46.53, C 14.67, H 2.48, Cl 15.66. Yield% = 70.

Au(dpma)₂Cl: Anal. $C_{30}H_{26}N_4S_4ClAu$. Calcd.: Au 24.06, C 44.74, H 3.50, Cl 4.40. Found: Au 25.04, C 43.92, H 3.64, Cl 3.81. Yield% = 90.

Physical measurements were made as previously described[1].

Polarographic measurements were recorded as previously described[7].

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