SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY SOUTH. BRAZ. J. CHEM., Vol. 15, No. 15, 2007

[Au-S₄]^Z AND [Au-O₂S₂]^Z – TYPE COMPLEX COMPOUNDS RELATED BY ELECTRON-TRANSFER REACTIONS

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ABSTRACT

The syntheses and the properties of square-planar $[Au-S_4]^z$ and $[Au-O_2S_2]^z$ – type complex compounds, involved in electron-transfer reactions, are presented. The complexes obtained are characterized by elemental analysis, IR, visible, UV, ESR spectroscopy, conductivity and polarographic data.

KEYWORDS: Gold (III), complex compounds, electron-transfer reactions

RESUMO

A síntese e as propriedades dos compostos quadrado-planares $[Au-S_4]^z$ e $[Au-O_2S_2]^z$, envolvidos em reações de transferência de elétrons são apresentadas e discutidas. Os complexos obtidos foram caracterizados por análise elementar, espectroscopia infravermelha, visível, RES, condutividade e medidas polarográficas.

PALAVRAS CHAVE: Complexos de Au(III), reações de transferência de elétrons

INTRODUCTION

An increasing number of papers published in recent years deal with description of syntheses and properties of complex compounds formed by various metallic ions with bidentate heterocyclic ligands (S₂), (N, S) and (O, S)¹⁻¹⁰.

The special interest aroused by these complexes is due, among others, to the fact that the complex compounds, readily participate in electron-transfer reactions without modifying the coordination geometry^{11, 12}.

The data reported in this paper referring to $[M-S_4]^z$ and $[M-O_2S_2]^z$ – type will contribute to enrich the knowledge in this field, as they refer to complex compounds of Au (III) with 6-nitro-quinoxaline-2,3-dithiol (NQDT), 6,7-dinitro-quinoxaline-2,3-dithiol (DNQDT), 2,3-dithiobenzo-quinoxalene-5,10-dione (DTBQD), 5,6-dithiobenzo-7,8-phenazine (DTBP) and 2-hydroxy-3-mercaptomethyl-1,4-naphthoquinone (HMMNQ)¹³.

EXPERIMENTAL PROCEDURE

Reagents: H[AuCl₄] (Merch,p.a.) and ligands (NQDT, DNQDT, DTBQD, DTBP, HMMNQ), double recrystallized (alcoholic solutions).

Instruments: The IR spectra (KBr) were recorded on a Perkin-Elmer FT-1600 Hewlett Pachard instrument.

An Unicam UV-visible 2-300 spectrophotometer was used to perform the electronic spectra.

The ESR spectra were recorded with an IFA Bucharest AR 7-5 spectrometer, working in the X band (9060 MHz) and having a 100 kHz modulation of the magnetic field.

The spectra were obtained at room temperature with a Mn (II) standard ($g_3 = 2.03584$, $g_4 = 1.98040$, $H_4 = 3268.5$).

The polarograms were recorded with an Orion KTS 7-77-4/b instrument. The halfwave potentials of the solutions (10^{-3} M) of complexes were measured at room temperature, using a calomel reference electrod and a dropping mercury electrode; a 10^{-1} M solution of tetra-n-butylammonium perchlorate was used a supporting electrolyte. The electrical conductivity was determined on a Conductivity meter OK 102-1 Radelkis.

Preparation of complexes: The $[(C_2H_5)_4N]$ $[Au(NQDT)_2]$ was prepared according the following procedure: 1 g of metallic sodium was dissolved in 50 ml absolute methyl alcohol and 1,4 g of freshly prepared and purified NQDT was added to the solution under stirring, until complete dissolution.

To the solution this obtained, 0,5 g of H[AuCl₄], was then added dropwise, during 18-20 minutes.

The solution was filtered, then the filtrate was treated with 1,5 g tetraethylammonium iodide, dissolved in a minimal amount of absolute mathanol.

The solution was allowed to stand for 5-6 hours.

Water was added until the first crystals appered. The product was filtered and dried under vacuum avernight.

All the other complexes have been prepared by a similar procedure.

RESULTS AND DISCUSSIONS

The complex compounds of Au (III) with the above-mentioned ligands are microcrystalline variously coloured substances, whose melting points are higher than that of the pure ligand (Table 1). They are stable in time, insoluble in the usual organic solvents and partially soluble in a hot mixture of methylene-cloride-absolute ethanol 1/1 (in volumes).

The results of the elemental analysis (Table 1), show that the complex compounds of Au (III) are of $R[AuL_2]$ – type, where $R = [(C_2H_5)_4N]^+$, L = NQDT, DNQDT, DTBQD, DTBP and $[AuL_2]Cl$ – type, where L = HMMNQ.

The formulations can be explained only if the dithiols act as bidentate ligands (S_2) , participating in the formulation of complexes as dithiolate dianions, gold having +3 oxidation state. In the case of $[AuL_2]Cl - type$ complex, HMMNQ acts as bidentate monoanionic ligand (O, S).

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				Analyses (%): Found/calcd.				
Compound*	Colour	M.p	Mol.**					
			cond.	Metal	С	S	Ν	Н
		°C	Ω^{-1} cm ² mol ⁻¹					
$R[Au(NQDT)_2]$	yellow	169	94.5	24.30/	36.71/	15.98/	12.98/	3.84/
	-			24.59	35.95	15.33	12.23	3.51
R[Au(DNQDT) ₂]	yellow-	173	96.3	21.12/	32.94/	14.88/	7.47/	2.83/
	orange			21.96	32.11	14.27	7.80	2.90
$R[Au(DTBQD)_2]$	orange	138	95.8	22.24/	44.72/	8.65/	14.33/	3.05/
				22.62	44.09	8.04	14.70	3.21
$R[Au(DTBP)_2]$	deep-	181	98.7	21.33/	52.08/	14.46/	7.49/	3.84/
	red			21.62	52.69	14.05	7.68	3.95
[Au(HMMNQ) ₂]Cl	dark-	147	94.9	29.15/	39.86/	9.92/		2.31/
	red			29.38	39.37	9.55		2.09

Table 1. Analytical and physical data of complexes

*) $R = [(C_2H_5)_4N]^+$; **) 10⁻⁴M DMF solution, 22°C

Table 2. Infrared spectra (cm⁻¹)

C 1*)									
Compound	U _{S-H}	$v_{C=O}$	$v_{C=C}$	v_{NO2}	v_{NO2}	v_{C-N}	υ _{C-H}	v_{2CH}	U _{C-S}
	valency		skeleton	asym.	sym.	$v_{C=N}$	plane	rocking	valency
	UO-H					valency	mation	TOCKINg	
NODE	valency		1(20	1560	1000	1070	10.00	0.15	(())
NQDT	2450	-	1620	1560	1330	1270	1060	845	660
	m		1	m	1	1	m	1	m
$R[Au(NQDT)_2]$	2100	-	1630	1520	1320	1210	1010	835	665
	W		v.i.	w	sh	sh	v.i.	v.i.	W
	2350								
	sh								
DNQDT	2360	-	1610	1565	1340	1270	1045	855	655
	m		i	i	m	m	m	m	m
$R[Au(DNQDT)_2]$	2350	-	1616	1550	1360	1240	1075	850	650
	sh		i	w	w	sh	v.i.	sh	w
DTBQD	2450	1660	1335	-	-	1270	1050	810	650
	m	i	m			v.i.	m	u	m
			1565						
			v.i						
R [Au(DTBQD) ₂]	2350	1650	-	-	-	1265	1040	835	645
	sh	i				m	w	m	w
DTBP	2350	1660	1355	-	-	1220	1050	855	685
	m	i	v.i.			i	i	v.i	m
			1585			1245			
			m			v.i			
R [Au(DTBP) ₂]	2328	1660	1620	-	-	1250	1065	845	665sh
	sh	i	sh			sh	m	W	
HMMNQ	3380	-	1545	-	-		1080	820	680
	m		i				m	m	i
			1590						
			m						
R[Au(HMMNQ) ₂]Cl	-	-	1540	-	-	-	1075	828	655
			i				W	m	sh
			1580						
			m						

*) $R=[(C_2H_5)_4N]^+$; v.i. = very intens; i = intense; m = medium; w = weak; sh = shoulder

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In an attempt to obtain data on the nature of the chemical bond¹⁴ in the complex compounds studied, we have recorded IR spectra both for pure ligands and for the corresponding complexes (Table 2).

The data presented in Table 2 show that the absorption bands due to vibrations of various groups, not involved in the coordination, appear in the infrared spectra of both free ligands and complex compounds in the same spectral domains, with unchanged or slighthy modified intensities. In the case of $[Au-S_4]^2$ – type complexes (L = NQDT, DNQDT, DTBQD, DTBP) the characteristic bands of the S-H groups, which appear in the IR spectra of the free ligands as shoulders at 2450 cm⁻¹, 2360 cm⁻¹ and 2350 cm⁻¹, are modified in shape in the spectra of complex compounds and are shifted, proving the involvement of such bands in the coordination process. It has also been found that, in the spectra of complex compounds the bands due to the vibration of C-S bonds are somewhat shifted and modifed, compared to the spectra of free ligands, and this is an additional evidence in favour of the coordination of dithiols by the S-H groups.

In the case of $[Au-O_2S_2]^z$ – type complex, $[Au(HMMNQ)_2]^+$ respectively, the disappearance of the 3380 cm⁻¹ vibration frequency of the O-H band can be noticed, proving the involvement of these group in the coordination. The characteristic band of S-H group, which appear in the spectra of the ligand as intense band at 680 cm⁻¹, in the complex spectrum appear at slightly modified frequencies, proving the involvement of these group in the coordination.

The geometry of the complex compounds obtained has been established by determining their visible and UV electronic spectra (Table 3).

able 5. Electronic spectra in the 6 v and visi							
Compound	$1/\lambda$ (cm ⁻¹)	Assignment					
[(C ₂ H ₅) ₄ N][Au(NQDT) ₂]	30840 37850 45420	${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$					
[(C ₂ H ₅) ₄ N][Au(DNQDT) ₂]	31270 38440 45270	${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$					
[(C ₂ H ₅) ₄ N][Au(DTBQD) ₂]	30980 37470 45290						
$[(C_2H_5)_4N][Au(DTBP)_2]$	30780 36850	${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$					
[Au(HMMNQ)2]Cl	30330 37300 45420	${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$					

Table 3. Electronic spectra in the UV and visible range

The bands observed in the electronic spectra of the complexes studied were assigned according to Gray and Ballhausen¹⁵ and Vanquickenborne¹⁶. They used to molecular orbital approach to explain the spectra of square-planar complexes of the d⁸ elements: Ni (II), Pd (II), Pt (II) and Au (III).

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The correspondence of these bands observed in the electronic spectra of Au (III) complexes with those of $[Au(CN)_4]^2$ promts us to assume the following assignments:

 ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g} \ [b_{2g}(\pi^{*}) \rightarrow b_{1g}(\sigma^{*})], \ (d-d);$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g} \ [b_{2g}(\pi^{*}) \rightarrow a_{1g}(\sigma^{*})], \ (L \rightarrow M \ charge \ transfer);$

 ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u} [b_{2g}(\pi^{*}) \rightarrow a_{2u}(\pi^{*})], (d-d).$

The correspondence of these bands observed in the prepared complexes, with the bands described for $[Au(CN)_4]^-$ leads to the conclusion that all these compounds have an analogous square-planar symmetry.

The study of the complex compounds has been completed with conductivity measurements (Table 1). These data show that the compounds investigated are electrolytes (1:1) with $\lambda = 94.5 - 98.7 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, in 10⁻⁴M DMF solutions, at 22°C. This data are close to the value of the electric conductivity of the known complex ion $[Au(TDT)_2]^2$, which is a 1:1 type electrolyte. These results are also in agreement with the oxidation state +3 of the gold, resulted from chemical analysis.

The complex compounds studied present no ESR signal, which agrees well with the supposed oxidation state +3 for gold.

The polarographic study (Table 4) of the complex combinations suggests the existence of the electron-transfer reactions, the following species can be obtained in this case:

$$[\operatorname{Au-S} 4]^{-} \xrightarrow{+e^{-}} [\operatorname{Au-S} 4]^{2-}$$
$$[\operatorname{Au-O} 2S_{2}]^{+} \xrightarrow{+e^{-}} [\operatorname{Au-O} 2S_{2}]^{-}$$

$$[\text{Au-O}_2\text{S}_2]^+ \underbrace{+\text{e}^-}_{-\text{e}^-} [\text{Au-O}_2\text{S}_2]^0$$

Compound	$E_{1/2}(V)$	$E_{1/2}(V)$	$E_{1/2}(V)$
$[(C_2H_5)_4N][Au(NQDT)_2]$	-0.380	-0.610	-0.945
$[(C_2H_5)_4N][Au(DNQDT)_2]$	-0.392	-0.80	-
$[(C_2H_5)_4N][Au(DTBQD)_2]$	-0.378	-0.75	-0.95
$[(C_2H_5)_4N][Au(DTBP)_2]$	-0.384	-0.628	-
[Au(HMMNQ) ₂]Cl	-0.284	-0.505	-

 Table 4. Polarographic data

The other observed waves are due to the reduction of the ligands. The data collected in connection with these complexes show that, aside from participating in electron transfer reactions, the evidenced species can also be obtained chemically, because the half-wave potentials range between +0.95 V and -0.95 V, a region in which oxidizing or reducing agents do not break un the complex.

CONCLUSIONS

Five new complex compounds of Au (III) have been with heterocyclic ligands. Chemical analysis and the results of physico-chemical determination suggest that these compounds are of the $[Au-S_4]^-$ - type for NQDT, DNQDT, DTBQD, DTBP and $[Au-O_2S_2]^+$ - type for HMMNQ, and exhibit square-planar geometry. Polarography data prove their involvement in the electron-transfer processes.

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The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com.

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