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THERMAL DECOMPOSITION OF TRIALKYL/ ARYLPHOSPHINE GOLD(I) CYANIDE COMPLEXES

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Abstract

Combined TG/DTA techniques have been used to study the thermal decomposition of R_3PAuCN (where *R* is ethyl, cyclohexyl, *o*-tolyl, *m*-tolyl, *p*-tolyl, allyl, cyanoethyl, 1-naphthyl and phenyl) complexes. It was observed that all of these complexes underwant decomposition cum redox reactions in the range of 200–600°C with evolution of both trans ligands, which are phosphine and cyanide, leaving metallic gold as a residue. The thermal decomposition of *o*-Tol_3PAuCN has revealed that this is a stepwise process. In the first step decomposition takes place with evolution of phosphine and generation of AuCN, which in second step undergoes a redox reaction to produce metallic gold. The DTA curves have also confirmed these results.

Keywords: alkyl/arylphosphine gold(I) cyanide, redox reaction, thermal decomposition

Introduction

Gold(I) drugs have been used in the treatment of rheumatoid arthritis (RA) for over 60 years [1–4]. Solganal (gold(I) thioglucose) and myochrysine (gold(I) thiomalate) are highly water soluble gold drugs and are only active by injection [1–3], whereas, Auranofin (1-thio-β-*D*-glucopyranose-2,3,4,6-tetracetato-S), (triethylphosphine) gold(I) is lipophilic and is an orally active drug [4].

Smokers who are treated with various anti arthritic gold(I) drugs have been reported to contain higher concentration of gold in their red blood cells as compared to non-smokers [5–7]. Tobacco smoke contains approximately 0.5 μg l^{-1} of HCN [8] which, interacts with these gold drugs to form L–Au–CN as an asymmetric complex (where *L* is a thiolate or phosphine group). The L–Au–CN complexes readily undergo disproportionation reactions in solution as shown in Eq. (1) to form $[Au(CN)_2]^-$ species, which can enter red blood cells.

$$2L–Au–CN \leftrightarrow [AuL_2]^+ + [Au(CN)_2]^- \quad (1)$$

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Similar disproportionation reactions have been observed in R_3PAuCN complexes in solution form, however in solid state these complexes have been identified as linear asymmetric [9–12] but we have isolated [CEP–Au–CN] complex as an ionic compound $\{[(CEP\}_2Au]^+[Au(CN)_2]^-\}$ [13]. Recently, we have prepared a series of R_3PAuCN complexes [14], and have studied their disproportionation reactions in solution using ^{13}C, ^{31}P and ^{15}N NMR spectroscopy. Since these gold complexes are very important from medicinal point of view therefore we decided to study their thermal stability in the present work, where no one else, to the best of our knowledge has reported these studies on R_3PAuCN complexes in the literature.

Experimental

Reagents

Ethanol, potassium cyanide, thiodiglycol, dimethylsulfide, $HAuCl_4 4H_2O$ and alumina were purchased from Aldrich, whereas, phosphine ligands (ethyl, cyclohexyl, *o*-tolyl, *m*-tolyl, *p*-tolyl, allyl, cyanoethyl, 1-naphthyl and phenyl) were obtained from Stream Chemical Company.

Synthesis of R_3PAuCN complexes

Two methods were used to synthesize R_3PAuCN complexes [10, 14–17], which are given below. Complex 1 was prepared from method-1, whereas complexes 2–10

Table 1 Elemental analysis, melting points and yields of R_3PAuCN and AuCN complexes

Complex	R_3P	Analysis/% found (calculated)			Melting point/°C	Yield/ %
		C	H	N		
1	$Cycl_3P$	44.80(45.32)	6.72(6.56)	2.63(2.85)	143	78
2	$CyclPh_2P$	46.45(46.44)	4.24(4.28)	3.01(2.89)	170	82
3	Et_3P	25.08(24.63)	4.54(4.40)	4.09(4.11)	108	73
4	Ph_3P	46.23(47.01)	3.29(3.09)	2.81(2.89)	202	90
5	$AllPh_2P$	43.12(42.76)	3.43(3.34)	3.03(3.12)	139	60
6	CEP	29.72(31.17)	2.95(2.34)	14.14(14.55)	121	71
7	Np_3P	58.56(58.58)	3.30(3.31)	2.35(2.20)	263	75
8	*p*-Tol_3P	50.08(50.09)	3.94(3.98)	2.81(2.66)	185	85
9	*m*-Tol_3P	50.05(50.09)	3.90(3.98)	2.75(2.66)	154	86
10	*o*-Tol_3P	51.06(50.09)	4.12(3.98)	2.93(2.66)	240	81
11	AuCN	5.41(5.38)	–	6.42(6.28)	–	70

Note: Full names of all phosphine ligands are given below: $Cycl_3P$ (tricyclohexylphosphine); $CyclPh_2P$ (cyclohexyldiphenylphosphine); Et_3P (triethylphosphine); Ph_3P (triphenylphosphine); $AllPh_2P$ (allyldiphenylphosphine); CEP (triscyanoethylphosphine); Np_3P (1-naphthylphosphine); *p*-Tol_3P (triparatolylphosphine); *m*-Tol_3P (trimetatolylphosphine); *o*-Tol_3P (triorthotolylphosphine)

were prepared from method-2. Elemental analysis, melting points and percentage yields of R_3PAuCN complexes are given in Table 1.

Method 1

The synthesis of R_3PAuCN complexes was a two-step reaction. In the first step Me_2SAuCl was prepared as a precursor complex by the reduction of $HAuCl_4$ with an excess of Me_2S [15] (Eq. (2)). While in the second step double displacement of Me_2S and Cl^- from Me_2SAuCl with phosphine and cyanide ligands was used to prepare R_3PAuCN complexes [14] (Eq. (3))

$$HAuCl_4+2Me_2S+H_2O \rightarrow Me_2SAuCl+Me_2SO+3HCl \quad (2)$$

$$Me_2SAuCl+R_3P+KCN \rightarrow R_3PAuCN+Me_2S+KCl \quad (3)$$

The reactions were carried out in darkness due to photodecomposition of Me_2SAuCl.

Method 2

The R_3PAuCN complexes were synthesized in two steps. In the first step R_3PAuCl was prepared by the reduction of $HAuCl_4$ with thiodiglycol at 0^oC, followed by the addition of R_3P ligand [17] (Eq. (4)). The R_3PAuCl prepared in this way was washed several times with ethanol to remove excess thiodiglycol to prevent further reduction of R_3PAuCl to metallic gold. In the second step Cl^- was replaced with CN^- from R_3PAuCl to synthesize R_3PAuCN [10, 16] (Eq. (5)).

$$R_3P+HAuCl_4+H_2O+S(CH_2CH_2OH)_2 \rightarrow R_3PAuCl+3HCl+OS(CH_2CH_2OH)_2 \quad (4)$$

$$R_3PAuCl+KCN \rightarrow R_3PAuCN+KCl \quad (5)$$

Synthesis of AuCN

The AuCN complex was synthesized in two steps. In the first step the $K[Au(CN)_2]$ complex was prepared by the double displacement of Me_2S and Cl^- from Me_2SAuCl with two equivalents of KCN [18] (Eq. (6)). Then, in the second step conc. H_2SO_4 was added in excess to $K[Au(CN)_2]$ complex, which resulted in the generation of AuCN complex [18] (Eq. (7)).

$$Me_2SAuCl+2KCN \rightarrow K[Au(CN)_2]+Me_2S+KCl \quad (6)$$

$$2K[Au(CN_2)]+H_2SO_4 \rightarrow 2AuCN+2HCN+K_2SO_4 \quad (7)$$

Thermal analysis

Thermal analysis in air atmosphere was carried out using a Netzsch simultaneous thermal analyzer STA 429, which measures TG and DTA simultaneously on the same sample.

In all runs, the sample (~20–30 mg) was placed in small platinum crucible. The crucibles were then mounted on a palladium–ruthenium platform on twin ceramic stems in such a way that the beads of two Pt/Pt–13%Rh thermocouples came within the base recess of each crucible. The platform was also connected to the microbalance such that slight change in the mass of the sample was indicated. Alumina was used as a reference material. The furnace was controlled at a heating rate of $10^{o}C\ min^{-1}$.

Results and discussion

The thermogravimetric (TG) curves of R_3PAuCN complexes are shown in Fig. 1 and the results are listed in Table 2.

Table 2 Thermogravimetric results of R_3PAuCN and AuCN complexes

Complexes	Mass loss/%		Temperature range/°C	Volatile matter	Residue
	found	calculated			
1	60.30	60.99	290–430	$Cycl_3P$, CN^-	Au
2	59.85	60.00	210–415	$CyclPh_2P$, CN^-	Au
3	42.00	42.56	255–405	Et_3P, CN^-	Au
4	58.64	59.54	280–490	Ph_3P, CN^-	Au
5	48.21	48.0	200–440	$AllPh_2P$, CN^-	Au
6	38.25	36.65	220–500	CEP, CN^-	Au
7	69.18	69.07	270–544	Np_3P, CN^-	Au
8	61.98	62.76	260–520	*p*-Tol_3P, CN^-	Au
9	61.87	62.76	220–500	*m*-Tol_3P, CN^-	Au
10	57.50	57.47	250–385	*o*-Tol_3P	AuCN
	5.51	5.29	385–480	CN^-	Au
11	11.5	11.65	350–700	CN^-	Au

All R_3PAuCN complexes except 10 showed a mass loss in the temperature range of 200 to $600^{o}C$ corresponding to the loss of alkyl/aryl phosphine and cyanide ligands in one step. The 10 complex showed two separate mass losses corresponding to the loss of tri-*o*-tolylphosphine ligand in first step and CN ligand in second step. Metallic gold was observed as a residue in the crucible in all the cases.

We also carried out thermal analysis of AuCN complex. It showed a gradual loss of CN ligand in the temperature range of 350 to $700^{o}C$ while metallic gold was observed as a residue in the crucible.

The DTA curves of R_3PAuCN complexes are also presented in Fig. 1. The 1–5, 7, 8, complexes showed two endothermic transitions, the first corresponding to their melting points and the second corresponding to the decompositions of these complexes with evolution of phosphine and cyanide ligands.

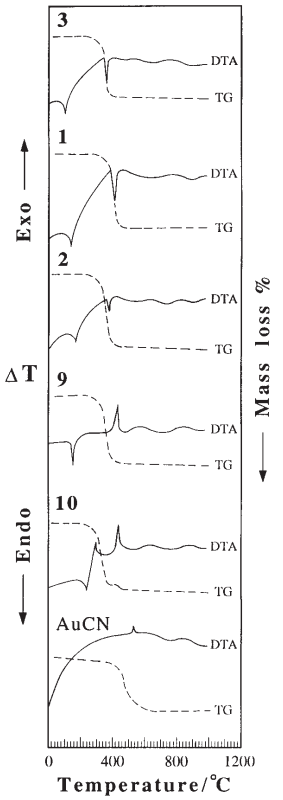

Fig. 1 TG/DTA curves of some R_3PAuCN complexes

The 9 complex, showed first endothermic transition corresponding to its melting point and second exothermic transition corresponding to the decomposition of the complex.

The 6 complex showed three endothermic transitions. The first endothermic transition at 121°C was observed due to melting of the complex, while the second endothermic transition at 286°C was observed due to decomposition of the complex and the third endothermic transition at 360°C was observed due to redox reaction of complex.

The 10 complex showed first endothermic transitions at 240°C corresponding to melting of the complex. While two more exothermic transitions were observed at 300 and 440°C corresponding to the decomposition and redox reaction respectively of the complex.

The AuCN complex showed only one exothermic transition at 531°C corresponding to its redox reaction. Combined TG/DTA results have given very useful information. These complexes undergo decomposition cum redox reactions with evolution of phosphine and formation of metallic gold as a residue. The decomposition of 10 complex has revealed that this process is actually stepwise. In the first step decomposition of complex results in the evolution of phosphine ligand and formation of

AuCN complex, which in the second step undergoes a redox reaction to form metallic gold. In case of 6 complex although TG showed complete loss of both triscyanoethyl phosphine and cyanide ligands in one step but DTA is able to identify these two different processes and give rise to two different endothermic transitions.

This thermal decomposition, coupled with redox reaction, can be shown through following Eqs (8) and (9). Since thermal analysis was performed in air atmosphere, therefore moisture present in air was responsible for redox reaction as shown in Eq. (9).

$$R_3PAuCN \rightarrow R_3P+AuCN \quad (8)$$

$$2AuCN+H_2O \rightarrow 2Au(O)+2HCN+1/2O_2 \quad (9)$$

Thermal degradation of AuCN has confirmed this finding because it also undergoes a loss of CN with a redox reaction to produce metallic gold as residue. However this loss of CN ligand has been observed over a broad range of temperature from 350 to 700°C, which can be explained on bases of polymeric nature of AuCN complex.

In our previous studies [14] it was observed that K_{eq} for disproportionation of R_3PAuCN complexes (Eq. (1)) was highly dependent on electronic properties (basicity) and steric factor (cone angle) of phosphine ligands. The electronic covalent parameter ν for various phosphines in $[R_3PNi(CO)_3]$ complexes was used by Tolman [19] to compare relative basicity of the phosphines. A decrease in the value of ν_{CO} indicates a net increase in the basicity of phosphines. All phosphine ligands have different basicity therefore they contribute different thermal stability to R_3PAuCN complexes, which results in decomposition of different R_3PAuCN complexes at different temperatures. The steric factor (i.e. cone angle θ) of phosphine ligands also plays an important role. In complex 10, *o*-Tol_3P has a once angle of 194°, which is highest of all phosphine ligands. This large value of cone angle makes complex 10 unstable therefore, it readily undergoes decomposition and redox reactions. The cone angle of *p*-Tol_3P and of Ph_3P is same i.e. 145°, therefore their thermal behaviour is comparable. Whereas cone angles of *o*-Tol_3P and *m*-Tol_3P are much higher than that of *p*-Tol_3P, therefore they exhibited different thermal behaviour. The values of ν_{CO} and cone angle for all phosphine ligands are given elsewhere [14].

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