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COORDINATION COMPOUNDS OF BIOLOGICAL INTEREST

THERMAL PROPERTIES OF THE COMPLEXES OF GOLD(III) AND SILVER(I) WITH DIETHYLDITHIOCARBAMIC ACID

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The thermal properties of the complexes of diethyldithiocarbamic acid, Et_2dtcH, with gold(III) and silver(I) were determined using TG, DTA, DRS and HTRS techniques. These compounds, contrary to the complexes obtained by the reaction of diethyldithiocarbamic acid with the transition metals, are not volatile. This behavior and their thermal stability, as determined by procedural decomposition temperatures, are discussed.

INTRODUCTION

Because of the analytical[1–4] and biological[5] interest of the complexes of diethyldithiocarbamic acid, Et_2dtcH, an attempt is made here to prepare the gold(III) and silver(I) derivatives and to study their thermal properties. These compounds were studied by thermogravimetry (TG), differential thermal analysis (DTA), high temperature reflectance spectroscopy (HTRS)[6,7], dynamic reflectance spectroscopy (DRS)[6,7] and IR spectroscopy.

EXPERIMENTAL

Instrumentation

The TG, DTG and DTA curves of the solid complexes were obtained by using a DuPont Model 990 DTA cell and console and a Model 951 thermobalance. The heating rate used was 10°C min^{-1} on samples whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of either dry nitrogen or air at flow-rates of 50–100 ml min^{-1}. All temperatures were corrected for thermocouple non-linearity and are, of course, procedural temperatures.

The HTRS and DRS curves of the complexes were obtained using a Beckman Model DK-2A spectroreflectometer equipped with a heated sample holder previously described[8]. White glass-fiber cloth covered with a thin cover glass was used as the reflectance standard. The sample holder atmosphere consisted of dry nitrogen and a heating rate of 10°C min^{-1} was employed for the DRS mode.

The IR spectra were recorded by means of a Beckman Model IR-12 instrument.

Preparation of the complexes

The silver compound, Ag Et_2dtc, was prepared by adding a 0.01 M solution of sodium diethyldithiocarbamate (Fisher) to a 0.01 M solution of silver nitrate (Merck) until a metal–ligand ratio of 1:1 was reached. A precipitate formed immediately and after stirring the mixture, it was filtered off, washed with hot water until free of the acid salt and dried for 48 h in a vacuum desiccator at room temperature.

The first gold compound, $Au(Et_2dtc)Cl_2$, was prepared in the same way but using a 0.1 M solution of gold(III) chloride (Fisher). The second gold compound, $Au(Et_2dtc)_3$, was prepared by adding a 0.01 M solution of gold(III) chloride to a 0.01 M solution of sodium diethyldithiocarbamate until the metal–ligand ratio was 1:5. The precipitate formed was treated as before.

RESULTS

Silver(I)-diethyldithiocarbamate

The TG and DTA curves of this yellow compound in air and in a nitrogen atmosphere are shown in Fig. 1.

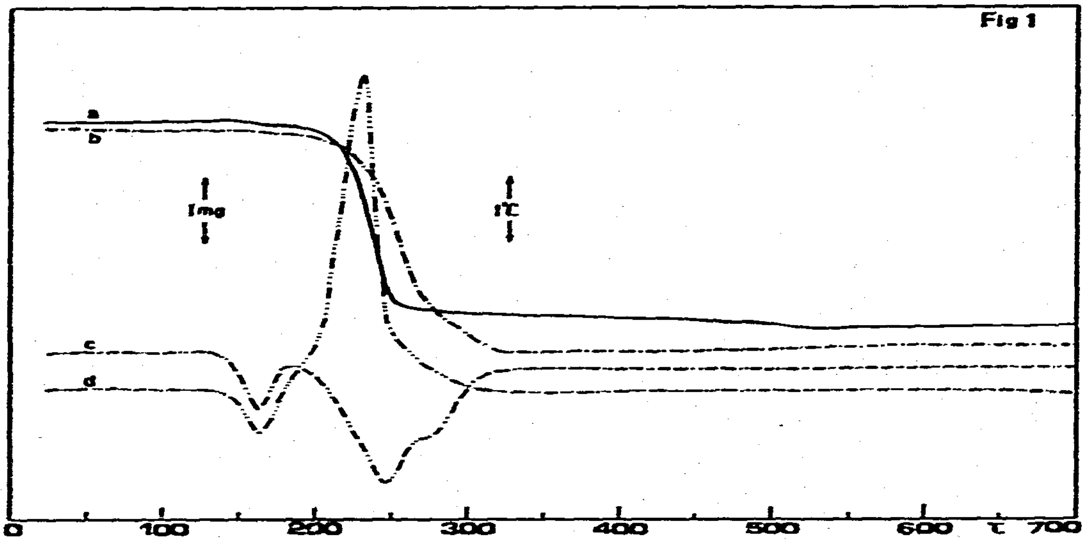


Fig. 1. TG and DTA curves of Ag Et_2dtc; (a) and (d) TG and DTA in air atmosphere; (b) and (c) TG and DTA in nitrogen atmosphere.

In air atmosphere, the compound exhibited a gradual mass-loss starting at about 150°C. The rate of decomposition increased up to about 190°C to give a break in the curve at which a mixture of Ag_2S, Ag_2SO_4 and Ag is obtained. The metal sulfide is then oxidized to sulfate in the range of 600–850°C and in the last step, between 825–925°C, the Ag_2SO_4 dissociates to metallic silver (42.12% calc.; 42.1% found). In a nitrogen atmosphere, the curve slowly deviates from the baseline starting at 150°C, and at 200°C, begins a decomposition process which proceeds through two unresolved steps to yield the sulfide, Ag_2S (48.38% calc.; 48.6% found).

The DTA curves in nitrogen and in air atmosphere show an endothermic peak at 165°C corresponding to a fusion transition and then a second endothermic peak in nitrogen (exothermic in air) corresponding to the decomposition reaction. In air there are two other peaks, the first of which is exothermic and corresponds to the formation of the metal sulfate; the second peak is endothermic and corresponds to the decomposition of the metal sulfate.

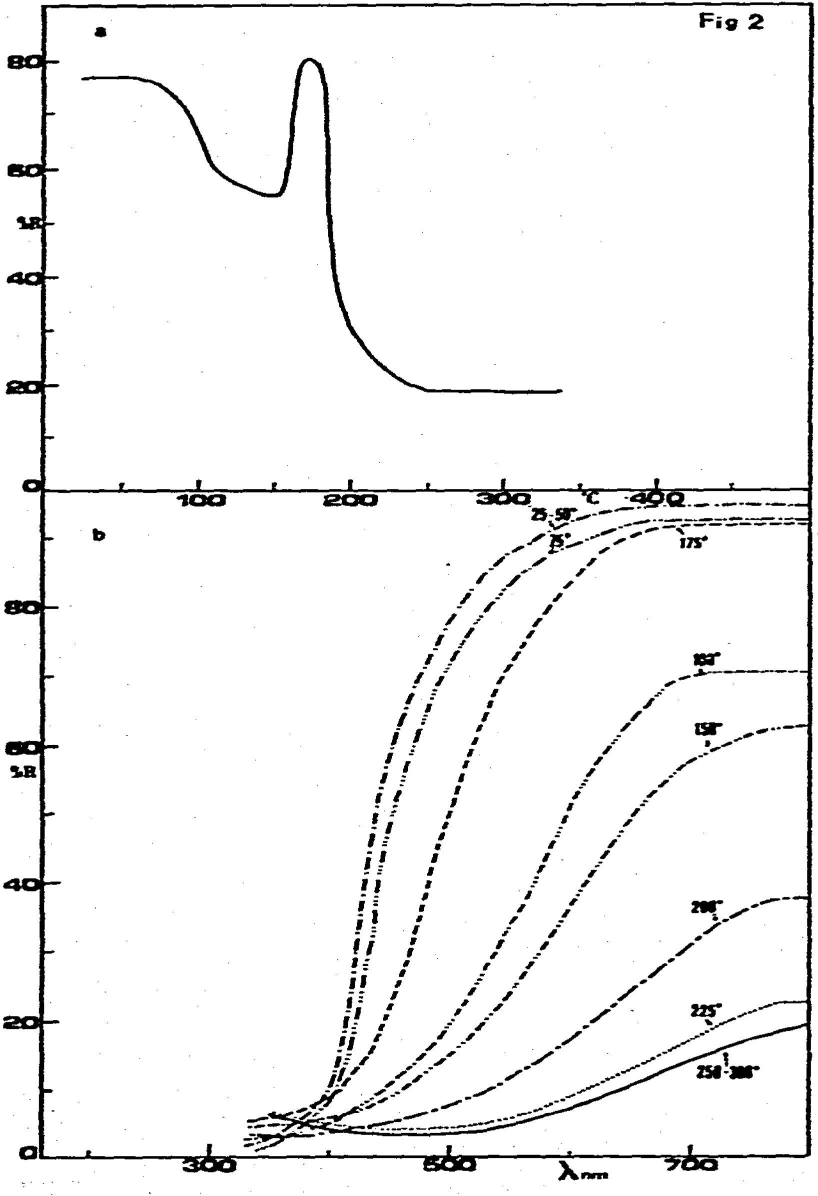


Fig. 2. DRS (a) and HTRS (b) curves of Ag Et_2dtc.

The HTRS and the DRS curves in nitrogen (Fig. 2) show a decrease in reflectance to 150°C; the reflectance then increases until the melting point of the compound and then decreases.

Gold(III)-diethyldithiocarbamate

This compound, $Au(Et_2dtc)Cl_2$, is yellow and precipitates in the anhydrous state, as shown by the TG and DTA curves in air and in nitrogen atmosphere (Fig. 3). In air atmosphere, the decomposition of the compound occurs in only one step starting at 195°C. Then there is a very slow mass-loss and at 700°C the curve reaches a plateau corresponding to metallic gold (47.35% calc.; 47.2% found). In nitrogen atmosphere, the decomposition goes through a two-step process starting at a somewhat higher temperature but still gives metallic gold as a residue. The DTA curve in air shows an endothermic peak partially overlapped by a second exothermic one. In a nitrogen atmosphere, the process occurs through a double endothermic peak which indicates that melting occurs along with the decomposition reaction.

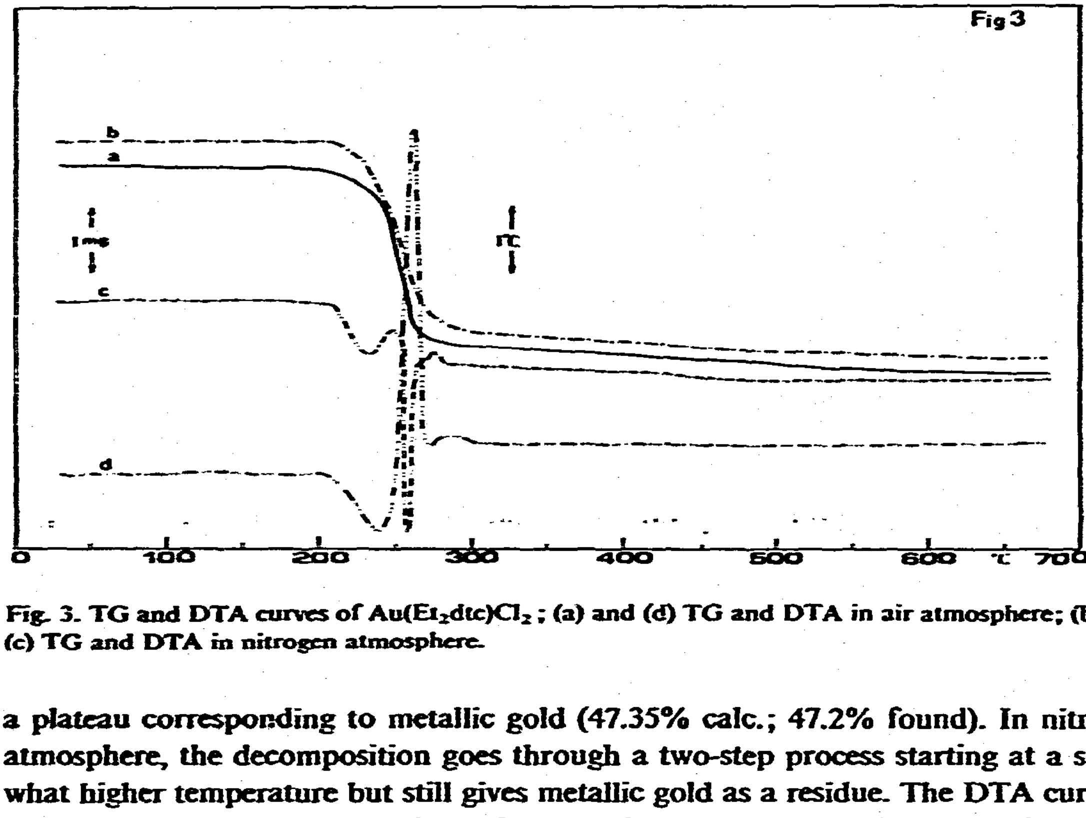


Fig. 3. TG and DTA curves of $Au(Et_2dtc)Cl_2$; (a) and (d) TG and DTA in air atmosphere; (b) and (c) TG and DTA in nitrogen atmosphere.

The DRS curve in nitrogen (Fig. 4) indicates a two-step process starting at 200°C and corresponding to the melting of the compound followed by its decomposition. This is confirmed by HTRS (Fig. 4) whose curves show a similar behavior. The spectrum obtained at 300°C is very low in reflectance due to the dark brown colored decomposition products.

Gold(III)-diethyldithiocarbamate

The TG and DTA curves in air and in nitrogen atmosphere are given in Fig. 5.

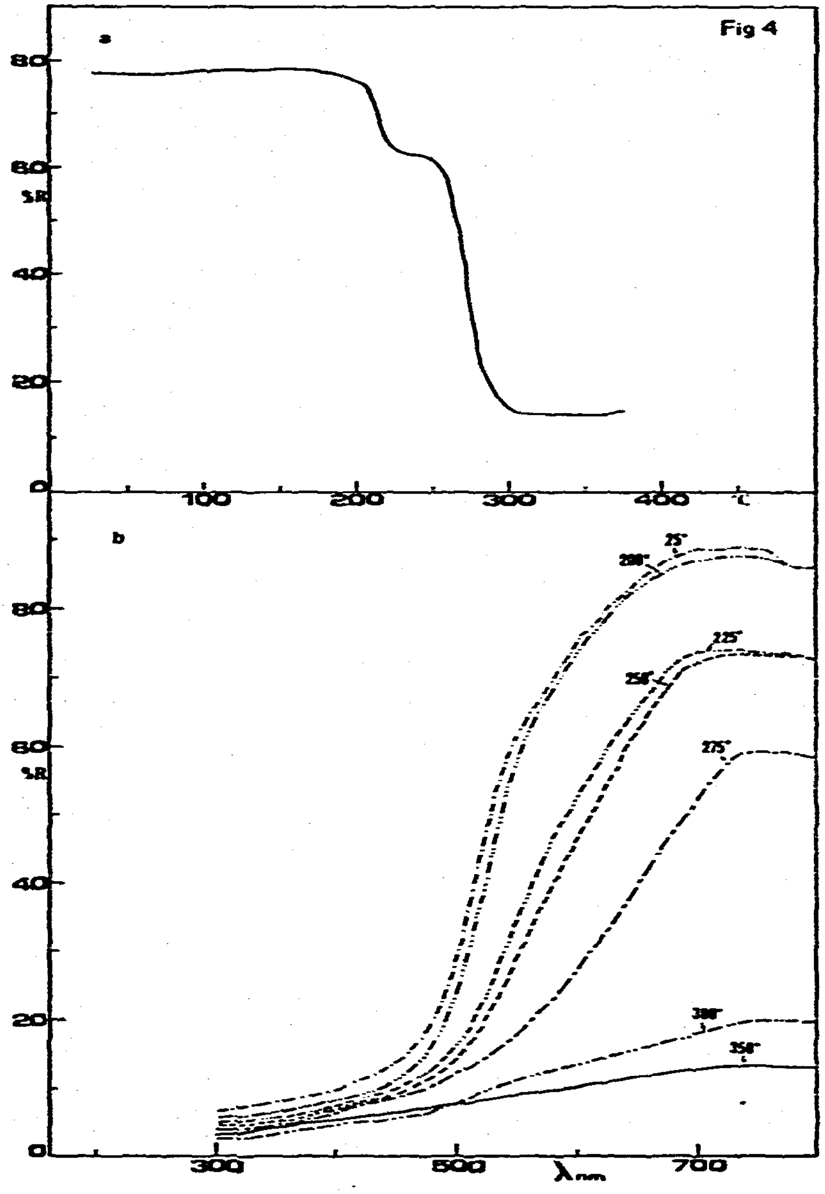


Fig. 4. DRS (a) and HTRS (b) curves of $Au(Et_2dtc)Cl_2$.

This black compound, $Au(Et_2dtc)_3$, is anhydrous and as shown by the TG curve, the decomposition reaction occurs by a two-step process starting at 150°C, to give a plateau at 255°C corresponding to metallic gold (30.72 calc.; 30.9% found). The DTA curves in air and in nitrogen show an endothermic peak at 73°C, corresponding to a fusion transition; this was confirmed by a cooling curve. The decomposition reaction in air gives an initial endothermic peak which is partially overlapped by an exothermic one. In nitrogen there is a doublet endothermic peak, the second of which

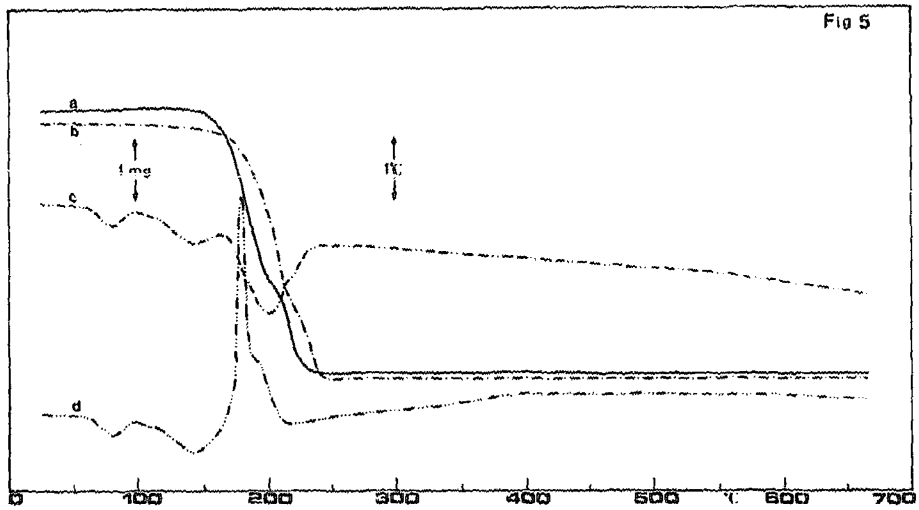


Fig. 5. TG and DTA curves of $Au(Et_2dtc)_3$; (a) and (d) TG and DTA in air atmosphere; (b) and (c) TG and DTA in nitrogen atmosphere.

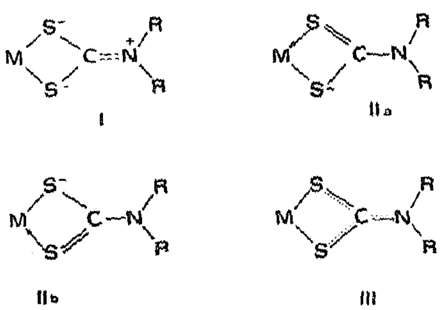
is asymmetric. This behavior is characteristic of a melting process with decomposition.

The DRS curve, in nitrogen (Fig. 6), indicates that the reflectance of the compound starts to decrease at 65°C, then reaches a plateau and successively begins to decrease again at about 150°C, the melting point temperature. The curve shows a maximum at 175°C, the temperature at which the decomposition reaction begins. The HTRS curves confirm this behavior and show a flat spectrum with a very low reflectance at 250°C because of the dark-brown decomposition products.

DISCUSSION

It is interesting to note that the compounds studied were not volatile, contrary to the analogous complexes of the transition metals[9,10]. According to Moshier and Sievers[11], compounds that are volatile at reasonably low temperatures do not have

Possible structures



large dipoles, nor do they exhibit adduct formation, polymerization or hydrogen bonding. On looking at the possible structures of the complexes of diethyldithiocarbamic acid, we can hypothesize that structures **I**, **IIa** and **IIb** give the maximum contribution to the electronic behavior of the ligand. From the C=N stretching frequencies (Table 1), according to Chatt[12] and Nakamoto[13], it can be seen that structure **I** is the most important. Considering the compounds where the ligand is the same, such as the complexes of the diethyldithiocarbamic acid, and where there is no change in the electron releasing ability of the $-N=R_2$ group, it can be seen that in agreement with Cotton[14], the type of metal ion (e.g., hard or soft acid) plays an important role in fixing the behavior of the complex and consequently the predominant structure. The shift of electron density from the conjugated ligand π bond to the metal ion is reflected in lower C=N and C=S frequencies, while the unavailability of suitable π-acceptor metal orbitals could result in high C=N and C=S frequencies as shown here in Table 1. This agress with structure **I** and hence the nonvolatility of these compounds. The position of the C=N stretching frequency also agrees with the thermal analysis data for the structure of these compounds[14]; the black $Au(Et_2dtc)_3$ is hexacoordinate while the yellow $Au(Et_2dtc)Cl_2$ is tetracoordinate. Looking at the thermal stability of the gold compounds, it can be seen that $Au(Et_2dtc)Cl_2$ is more stable than $Au(Et_2dtc)_3$, whose stability is lower than that for Ag Et_2dtc. As discussed earlier[15], this behavior can be explained on the basis that the intermolecular bonds of the lattice of the complexes having strong covalent metal–ligand bonds are weaker than those existing in complexes in which the metal–ligand bond has a higher ionic character. The higher ionic character of the chloride with respect to the diethyldithiocarbamic ion justifies the higher thermal stability of $Au(Et_2dtc)Cl_2$ with respect to that of $Au(Et_2dtc)_3$. At the same time, the greater tendency of the silver ion to accept electrons increases the ionic character of the ligand which increases the intermolecular bonds and hence the thermal stability of the Ag Et_2dtc, which is higher than that of $Au(Et_2dtc)_3$.

TABLE 1

PERTINENT IR FREQUENCIEES FOUND IN KBr PELLETS

Compound	ν *(C=N) (cm^{-1})*	ν *(C=S) (cm^{-1})*
Ag Et_2dtc	1505	610
$Au(Et_2dtc)Cl_2$	1590	620
$Au(Et_2dtc)_3$	1540	625

Looking at the possible analytical application of these compounds to the gravimetric analysis of the silver and gold, it can be seen that:

(a) $Au(Et_2dtc)Cl_2$ is useful for the heterometric determination of gold[1] but not for gravimetric analysis because of the formation of a soluble ion, $Au(Et_2dtc)_2^+$. It is impossible, however, to obtain it pure in the solid state when the ligand:metal ion molar ratio becomes higher than 1.

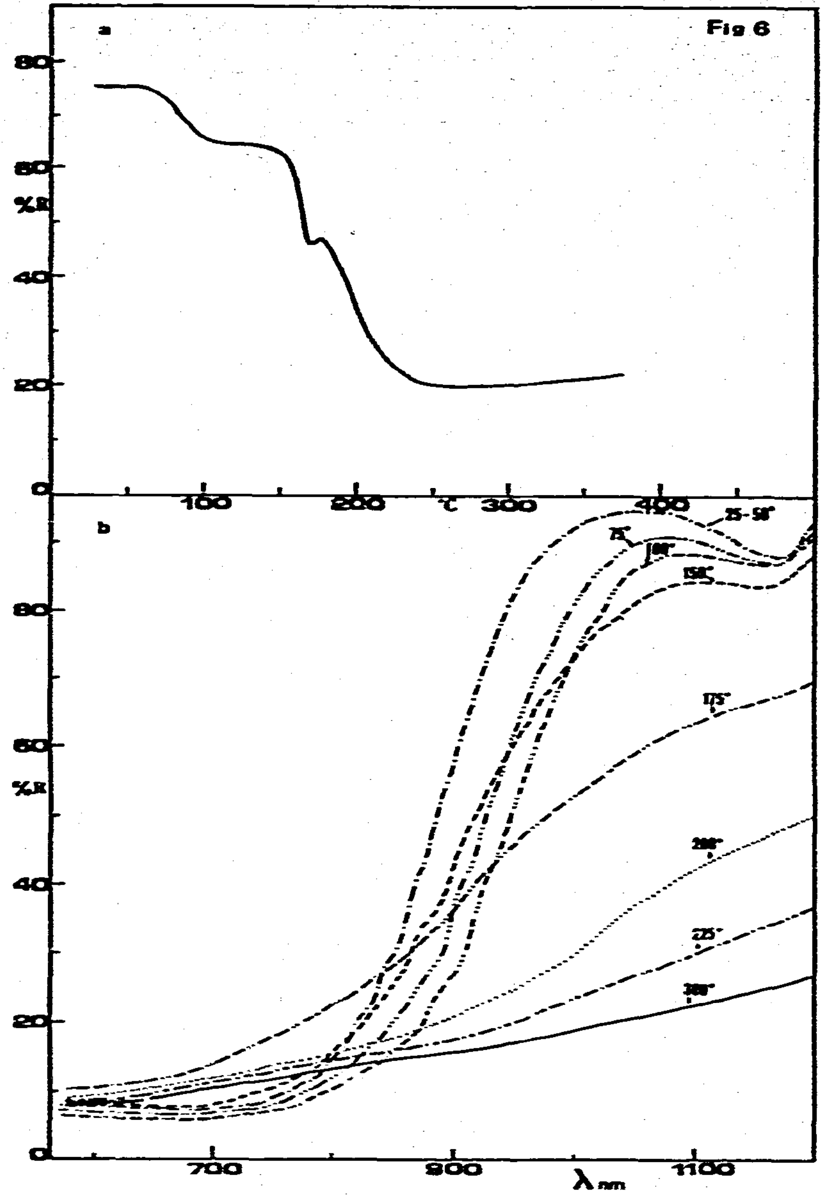


Fig. 6. DRS (a) and HTRS (b) curves of $Au(Et_2dtc)_3$.

(b) The compounds, $Au(Et_2dtc)_3$ and $Ag\ Et_2dtc$, are not useful for the gravimetric analysis of gold and silver because their precipitation is not quantitative.

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