研究論文

Synthesis, Characterization and Explosive Properties of Picramates of Palladium and Uranium

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Summary

Picramates of palladium and uranium were prepared by treating the aqueous solutions of palladium chloride and Uranium nitrate with sodium picramate. A metal : ligand ratio of 1 : 2 was established in all the cases with the help of micro-analysis and confirmed by spectrophotometric, potentiometric and conductometric studies. I. R. studies indicate $H_2N \longrightarrow M$ coordination, where M is palladium or uranium. Explosive properties of these picramates indicate that palladium picramate is thermally more stable than uranyl picramate.

1. Introduction

From the point of view of explosives, the interest in nitrophenols has centred chiefly around symmetrical trinitrophenol, commonly as picric acid while metal picrates and their explosive properties have been extensively studied by a number of workers[1]. In the case of lead salts of certain polynitrophenols, Glowiak[2] reported that the substitution of one of the $-NO_2$ groups by $-NH_2$ group results in an increase in sensitiveness to impact and flame. Therefore, picramic acid (2-amino-4,6-dinitrophenol) is of considerable interest. Agrawal and Agrawal[3]-[5] studied the chemistry of the picramates of iron, cobalt, nickel, copper, silver, zinc, cadmium and mercury rather extensively. In an earlier paper we have reported the picramates of titanium, zirconium and thorium[6]. However, hardly any work seems to have been carried out on the picramates of palladium and uranium whose synthesis, characterization and explosive properties form the subject matter of this paper.

2. Sample and Experimental Technique

All the chemicals were obtained from B. D. H. and were of analytical grade except palladium chloride which was a Johnson Mathey Chemicals product.

Sodium picramate was prepared by suspending a known weight of picramic acid in distilled water and then treating it with an equivalent amount of sodium bicarbonate solution. The resulting mixture was digested on a water bath to ensure complete reaction. On cooling, the product was filtered and washed with ice-cool water. Red shining crystals of sodium picramate obtained.

The metal picramates could be easily precipitated by adding a solution of the sodium picramate to a solution of a salt of these metals. Thus, the picramates were precipitated from 0.02 M solutions of palladium chloride and uranyl nitrate by adding a 0.02 M solution of sodium picramate to each of them. In every case the mixture was kept overnight to achieve equilibrium. Next day, the products were filtered and washed with water followed by ethanol. The samples were dried in a vacuum desiccator to constant wei ght and analysed for their con stituents. Results of micro-analyses are given in Table 1.

Spectrophotometric (visible) studies were carried out with the help of a Unicam SP 8000

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Table 1 Analytical Data for Metal Picramates

Formula*	% Metal	% Nitrogen	% Water
$Pd[C_6H_2(NO_2)_2(NH_2)O]_2H_2O$	Calcd. 20.4	16.1	3.5
	Found 20.0	16.8	4.0
$UO_2[C_6H_2(NO_2)_2(NH_2)O]_2H_2O$	Calcd. 34.8	12.3	2.7
	Found. 35.2	11.9	3.2

* Satisfactory carbon and hydrogen analyses have been obtained for all the compounds.

recording Spectrophotometer and a Unicam Spectrophotometer Number 23704. Job's continuous variation method[7] was employed.

The pH measurements were carried out with a Leeds and Northrup Co (Philadelphia, U.S.A.) pH meter.

The electrical conductance of the solutions were measured with a Toshniwal's Conductivity bridge (type CL01/02) at 30 ± 1℃. Job's monovariation method[7] was employed to determine the compositions of these picramates.

I.R. spectra of the compounds were recorded with the help of a Perkin-Elmer Infrared Spectrophotometer model 337 using KBr pellet technique in the range of 400-4000 cm^{-1}.

3. Explosive Properties

The compounds used for the measurements of explosive properties were dried at 100-110℃ for 2-3 hours to constant weight.

The explosive properties viz. Explosion Delay[8], Explosion Temperature[9], Thermal Sensitivity[10] and Explosion Pressure[11] were measured in a manner similar to that reported in our earlier communication[7].

Explosion Delay

Explosion delay was measured by the method of Copp et al[8]. Approximately 20 milligrams of the sample were placed in a pyrex tube which was suddenly plunged into a paraffin liquid bath maintained at 320±2℃. The time interval between insertion and the moment of explosion was noted with stop watch. This gave the value of explosion delay. A mean of three readings was taken as the final reading (values given in Table 2).

Explosion Temperature

This is taken as the temperature necessary to cause explosion in exactly 10 seconds, when a thin-walled pyrex tube containing a few milligrams of the sample is dipped to a constant depth into a potassium hydrogen sulphate bath. The method has been described by Weber[9] and extensively used by Agrawal et al[5]; readings are recorded in Table 2.

Table 2 Explosion Delay and Temperature for the Picramates

Compound	Explosion delay at 320℃ (sec)	Explosion temperature for explosion delay of 10 sec. (K)
Palladium picramate	52.5	671±2
Uranyl picramate	14.8	617±2

Thermal sensitivity

The thrmal sensitivity of an explosive is related to the activation energy, E, of the physicochemical procses controlling the explosion delay, DE. The relationship[10]

$$\log D_E = \frac{E}{4.56T} + B$$

holds good (T°K is the temperature of the both in which the experiment is carried out and B is a constant). Curves obtained by plotting D_E

against 1/T are given in Fig. 1. The value of

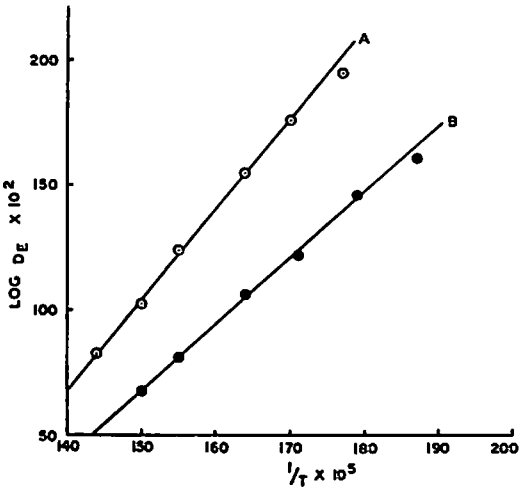

Fig. 1 Variation of log D_E with reciprocal of acsolute temperature
A=Palladium Picramate
B=Uranyl Picramate

E obtained with the help of these curves are shown in Table 3.

Table 3 Values of E and B for Different Metal Picramates

Compound	Activation Energy(E) (kJ/mol)	Constant B
Palladium picramate	88.1	-5.8
Uranyl picramate	56.5	-3.7

Explosion Pressure

Explosion pressure was measured by a method similar to that employed by Yoffe[11] for studying the thermal decomposition of azides. Instead of silicone oil, potassium hydrogen sulphate was used in the bath in which the explosion was carried out. The results obtained are recorded in Table 4.

4. Results and Discussion

On the basis of their microanalyses and spectrophotometric, potentiometric and conductometric studies it follows that the general formula for the metal picramates under study can be written as :

$$[C_6H_2(NO_2)_2(NH_2)O]_2M$$

Table 4 Explosion Pressure* of Metal Picramates (Density of mercury= 13.595 g/ml ; gravitation acceleration (g)=980.665 cm/sec^2

Compound	Height(H) (metre)	Explosion pressure (bath temperature) 350±2℃ (Nm^{-2} x 10^3)
Palladium picramate	0.1172	15.6
Uranyl picramate	0.0620	8.3

* Explosion pressure was obtained by taking 10mg of the explosive compound.

where M stands for Pd (II) or UO_2((II). Absorption associated with -NH deformation mode[12] are expected to appear near 1600 cm^{-1}. It is greatly masked by the other strong absorption in the same region. The -NH rocking and twisting modes[13], which appear as a doublet in the free ligand completely disappear in the spectra of these complexes indicating the presence of $H_2N\longrightarrow M$ coordination.

The appearance of -NH stretching vibration frequecy at 3075 cm^{-1} (for palladium picramate) and 3240 cm^{-1} (for uranyl picramate), as compared to 3400 cm^{-1} in the spectrum of sodium picramate, also indicates the presence of $H_2N\longrightarrow M$ coordination. This is in agreement with the view given by other workers[13][14].

The -OH stretching frequency of picramic acid, which occurs at approximately 3475 cm^{-1} is lowered due to the intramolecular hydrogen bonding between the -OH and the $-NO_2$ groups which occupy ortho positions to each other. However, the hydrogen bonding completely disappears in the complexes due to the ionization of the labile hydrogen and coordination of negative oxygen with the metals.

A band in the region 3400-3600 cm^{-1} in the spectra of sodium picramate and all the complexes is attributed to the water molecule present and has little effect on the spectra[15].

In addition to these bands, absorption bands are also present at 545 cm^{-1} (palladium picramate) and 495 cm^{-1} (uranyl picramate) which

may be assigned to the metal-nitrogen stretching modes analogous to the metal-nitrogen stretching modes in metal glycine complexes assigned by Nakamura[16].

On the basis of the data of explosive properties it can be concluded that the palladium picramate is thermally more stable than the uranyl picramate. Walsh[17]~[19] observed that for a given band the force and energy decrease and the length increases with increasing polarity. The thermal stability may, therefore, increase with decrease in ionic radius or increase in ionization potential. The results of Yoffe and coworkers[20][21] on inorganic azides and cyanamides lead to similar conclusions.

There is one interesting point which may be noted in the case of uranyl picramate. The radius of action of the uranium atom in a uranyl (VI) complex is approximately 0.90 Å[22]. This value is higher than that of palladium (II) (0.50 Å). And it can be easily seen from Tables 2-4 that the uranyl picramate is thermally less stable than the palladium picramate.

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パラジウムおよびウランのピクラミン酸塩の合成，特性および爆発性能

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塩化パラジウムおよび硝酸ウランの水溶液をピクラミン酸ナトリウムと反応させることによりパラジウムおよびウランのピクラミン酸塩を合成した。微量分析法や分光光度法，電位差法および導電率法による研究から，金属：リガンド比はいずれの場合も 1：2 であることを確かめた。IR による研究から，$H_2N \rightarrow M$ の配位（M：パラジウムまたはウラン）が示される。これらのピクラミン酸塩の性能試験から，ピクラミン酸パラジウムはピクラミン酸ウランに比べて熱的に安定であるといえる。

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