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Note on Structural Studies on *Pd*(II) and UO_2(II) Picramates

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Abstract. Structure of the picramates of *Pd*(II) and UO_2(II) have been studied with the help of molar conductance, magnetic susceptibility, electronic, infra-red ^1H-NMR spectra and TG studies. These studies indicate that the *Pd*(II) picramate is square planar and UO_2(II) picramate is octahedral, involving covalent bonding through the phenolic oxygen and coordination through the nitrogen of amide group.

1. Introduction

Transition metal picramates have attracted much attention as possible explosives. Taking into consideration of their explosive properties several transition metal picramates were synthesized and characterized[1–7]. Recently[8] we prepared the picramates of *Pd*(II) and UO_2(II). These picramates were characterized by microanalyses, conductance, pH, spectrophotometric and IR studies. A number of their explosive properties were also studied. However, we could not assign the structure of these complexes. In this paper we are reporting an investigatory study of the structure of these complexes.

2. Experimental

All the chemicals used were of analytical grade or equivalent quality. Metal picramates were prepared following the method reported earlier[7,8].

Conductometric titration and molar conductance measurements were made on a Toshniwal's conductivity bridge (type CL01/01, at 298°K. Magnetic susceptibility measurements were carried out by Gouy's method at room temperature (303°K). Mercury tetrathiocyanato cobaltate (II) was used for calibration. Electronic spectra were recorded on Unicam SP 8000 UV spectrophotometer in Nujal Mull. Infrared spectra of the ligand and the complexes were taken in *KBr* in the range 400–4000 cm^{-1} using Perkin-Elmer (model 337) spectrophotometer. ^1H-NMR spectra of ligand and complexes were recorded on Varian A-60 D.

Thermogravimetric analyses of the complexes were done with the help of a manual thermogravimetric analyser supplied by Planning and Development Division, Fertilizer Corporation of India, Sindri, Bihar. The initial weight of the sample was 0.210 g. The rate of heat was kept at 4°C/minute.

3. Results and Discussion

The molar conductance of the picramates of *Pd*(II) and UO_2(II) in acetone show that the complexes are non-electrolytes. The absence of anion in the complexes clearly indicates the formation of covalent bond between the metal and the phenolic oxygen. All the complexes are insoluble in water, ethanol and benzene and are soluble in DMSO giving deep red solutions probably due to destruction of the original structure.

The magnetic and spectral properties of *Pd*(II) and UO_2(II) complexes were studied to understand the spatial arrangement of the ligand molecules around the central metal ion.

As expected the *Pd*(II) complex is diamagnetic. The spectrum of this complex does not show the presence of spinforbidden transition. Only spin-allowed bands are exhibited at (cm^{-1}) : 25000 ($1A_{1g} \rightarrow 1A_{2g}$, $1E_g$) and 30000 ($1A_{1g} \rightarrow 1B_{1g}$) alongwith the two charge-transfer bands at 37000 and 48000 cm^{-1} with the transitions $1A_{1g} \rightarrow 1A_{2u}$, $1E_u$ and $1A_{1g} \rightarrow 1E_u$ respectively. Therefore *Pd*(II) picramate is square planar.

The UO_2(II) complex is diamagnetic, which is in accordance with f° configuration for the *U*(VI) ion. In the spectrum of UO_2(II) picramate, the charge transfer bands appear as strong peaks at 23809 cm^{-1} and 30000 cm^{-1}. On this basis, it is proposed that UO_2(II) picramate has octahedral structure with $O = U = O$ group lying perpendicular to the plane.

The IR spectrum of the ligand shows two bands at 3400 and 3320 cm^{-1} due to the asymmetric and symmetric —NH stretching frequencies of the $-NH_2$ group, respectively. A comparison of the IR spectra of the complexes with that of free ligand shows negative shift of the order 20–50 cm^{-1} and 15–60 cm^{-1} in these modes respectively, indicating coordination through the amide nitrogen. The disappearance of the $-OH$ frequency in the complexes as compared to the ligand indicates covalent bonding with the metal through the phenolic oxygen.

The ^1H-NMR spectrum of the free ligand exhibits two signals at $\delta = 7.70$ (OH) and $\delta = 8.2$ (NH_2), 1 and 2 in intensity. The signals are broad and show a significant down-field displacement in the complexes. In the spectrum of complexes of the *Pd*(II) and UO_2(II) a singlet of intensity 2 occurs at $\delta = 2.50$, due to the $-NH_2$ protons. The shift of the $-NH_2$ proton resonance observed upon coordination and the relative intensity of the signals are in agreement with direct interaction between the metal and the amide nitrogen.

The TG Curves (Fig. 1) indicate that the *Pd*(II) picramate explodes at 270° whereas, UO_2(II) picramate does not explode even above 400°. As evident from the TG curve in the latter case loss in weight upto 180° is accompanied by some decomposition. A change in curve between 180°–300° gives a clear indication of the

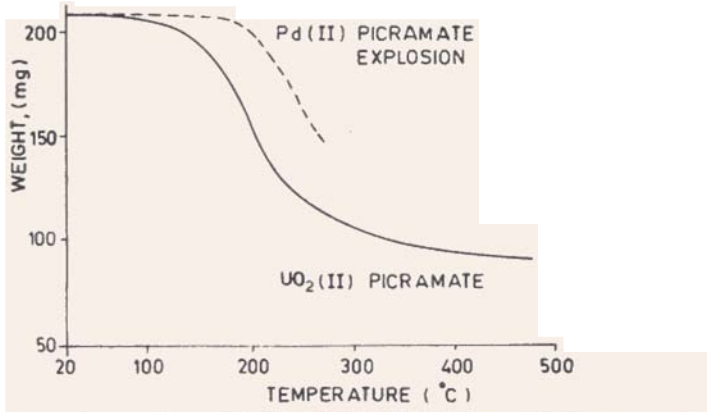

Figure 1. Thermogravimetric analysis of *Pd*(II) and UO_2(II) picramates.

complete decomposition of the dark-brown Uranyl picramate to brown-black Uranium oxide (UO_2). After 300° a nearly constant weight of the uranium oxide formed shows that the complex has been completely decomposed between 180°–300°. In the case of *Pd*(II), the initation of decomposition occurs at higher temperature than in the case of UO_2(II). The palladium complex explodes at around 270° while the uranyl complex decomposes smoothly between 180° and 300°. Other data connected with the explosive properties viz. explosion delay, explosion temperature and activation energy reported earlier[8] also support this fact.

The studies indicate that *Pd*(II) picramate is square planar and UO_2(II) picramate is octahedral, involving coordination through the nitrogen of amide group and covalent bonding through the negative oxygen.

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