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STUDIES ON METAL SALTS OF 4-(2,4,6 - TRINITROANILINO)BENZOIC ACID

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ABSTRACT

Synthesis, characterization and thermal studies of copper and lead salts of 4-(2,4,6-trinitroanilino)benzoic acid have been carried out. Differential thermal analysis data show that Pb^{2+} and Cu^{2+} salts are stable up to 240 and 260°C respectively and then decompose exothermically. Impact sensitivity value (h_{50}) is 77 cm for lead salt and 170 cm for copper salt. Both the salts are found friction insensitive upto 36 kg. The calorimetric values of lead and copper salts are 679 and 839 cal/g, respectively.

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INTRODUCTION

Metal salts of carboxylic acids are generally used as energetic ballistic modifiers in double-base and modified double-base propellants to increase burn rate and induce platonisation effect. Basic lead salycylate, lead stearate etc. are well known[1] examples. Salts of aliphatic carboxylic acids are effective in cool double base formulations while that of aromatic carboxylic acids in hot formulations[2]. The organic part in the metal salts of carboxylic acids cited above is inert and tend to bring down the energetics of the system. Carboxylic acids containing groups like nitro would increase the total energy output. Thus, it was of interest to synthesize metal salts of carboxylic acids which contain a picrylamino moiety. This paper presents the synthesis, characterization and thermal studies of lead and copper salts of 4-(2,4,6-trinitroanilino)benzoic acid (TABA).

EXPERIMENTAL

Materials

Laboratory grade picric acid, pyridine,

phosphoryl chloride, hydrochloric acid, lead nitrate and copper nitrate were obtained from commercial sources and used as received. Solvents used were laboratory grade benzene, ethylacetate and ethyl alcohol purified before use.

Synthesis

TABA and the two salts were synthesized as per Scheme 1.

4-(2,4,6-Trinitroanilino)benzoic acid (1): Into a three-necked one-litre round-bottom flask fitted with condenser and stirrer, 500 ml of 50 % aqueous ethanol were added. To it were added 25 g (0.1 mol) picryl chloride(1), 13.7 g (0.1 mol) *p*-aminobenzoic acid and 10.6 g (0.1 mol) sodium carbonate. The mixture was maintained at 70-75°C for half an hour under constant stirring and then cooled to room temperature, when a solid separated. This product was filtered to remove alcohol, dissolved in the minimum amount of distilled water, and neutralized with dilute HCl, when the desired product separated out. It was filtered using a Buchner funnel, dried, and recrystallized from

ethyl acetate. The yield was 30 g (85 %); m.p. 303°C (reported 304°C).[3]

Synthesis of Cu^{2+} and Pb^{2+} Salts of TABA(2): To a stirred aqueous solution of the sodium salt of TABA, maintained at 50-60°C, was added an aqueous solution of metal nitrate. The corresponding metal salt precipitated out. The salt was stirred for an additional 15 minutes, filtered, washed 2-3 times with water followed by alcohol, and dried in air to constant weight.

Infrared (IR) spectra of TABA and its salts were recorded on a Perkin-Elmer FTIR- 1605 spectrophotometer in KBr matrix. The metal contents were estimated by standard methods.[4] DTA curves were obtained on a locally fabricated equipment. The heating rate employed was 10°C/min and the mass of the sample was 10 mg. Density of the salts were measured by the flotation method. Calorimetric values of the salts were determined using a Parr adiabatic bomb calorimeter. Impact sensitivity of these salts were determined by a locally fabricated drop hammer(2.0 kg weight) apparatus. The friction

sensitivities were determined using a Julius Peter apparatus.

RESULTS AND DISCUSSION

The metal content results confirm the structure assigned to the Pb^{2+} and Cu^{2+} salts of TABA, viz. $Pb^{2+}(C_{13}H_7N_4O_8)_2^-$ and $Cu^{2+}(C_{13}H_7N_4O_8)_2^-$. The calculated lead and copper content for these salts are 23.02% and 13.88% respectively. The experimental values obtained were more than 99% of theoretical. The IR spectra of TABA and its salt are given in Figs. 1 & 2 respectively. The spectral assignments are compared in Table 1. The carbonyl frequency in TABA appearing at 1674 cm^{-1} shifts to 1654cm^{-1} in the salts. The latter is in conformity with the frequency of carboxylate anion, which is formed during salt formation. The carboxylate anion absorbs at a lower wave number than the carbonyl absorption because of the resonance of the negative charge between the two oxygen atoms. Thus the IR spectra confirm the formation of lead and copper salts.

TABLE 1

Important IR Spectral Assignments of TABA and Salts

Functional Group	Wave Number (cm^{-1}) TABA	Lead salt	Copper salt
O-H Stretching	3600	---	---
N-H Stretching	3380	3432	3316
C=O/Carboxylate	1674	1654	1654
NO2 asym.	1534	1534	1534
NO2 Sym.	1348	1348	1344

The impact sensitivity of the lead and copper salts was found to be 77 and 170 cm, respectively. For comparision, the impact sensitivities of the common explosives RDX and PETN, determined under identical conditions and apparatus are 55 and 43 cm, respectively; and, their friction sensitivities are 22 and 18 kg, respectively. Both the salts were found to be friction insensitive upto 36 kg.

DTA curves (Fig. 3) show that TABA and its Pb^{2+} and Cu^{2+} salts are stable upto 300, 260, and 240°C respectively and then decompose exothermically. The temperature of initiation of thermal decomposition (T_i) and peak maximum of the exotherm (T_{max}), respectively

for TABA and its salts are as follows : TABA, 300 and 340°C; Pb^{2+} salt of TABA, 260 and 280°C and Cu^{2+} salt of TABA, 240 and 265°C . This pattern follows the expected order of thermal stability based on the percentage ionic character of the metal-oxygen bond which is in the sequence Pb-O > Cu-O, as seen from the electronegativities of the participating atoms.[5] TABA and Pb^{2+} and Cu^{2+} salts of TABA each shows a second exotherm at 500, 438 and 441°C, respectively probably due to oxidative degradation. The densities of the salts were found to be 1.32 g/cc for Pb^{2+} and 1.26 g/cc for Cu^{2+} salts. Both the salts were found to have no free acid in them as evidenced by the neutral pH of the water washing.

CONCLUSION

Synthesis of two new energetic ballistic modifiers namely Pb^{2+} and Cu^{2+} salts of TABA has been reported. The thermal and calorimetric data indicate that these salts are energetic in nature. It has been found that both the salts are thermally stable. It is

also found that both the salts are insensitive to friction and impact.

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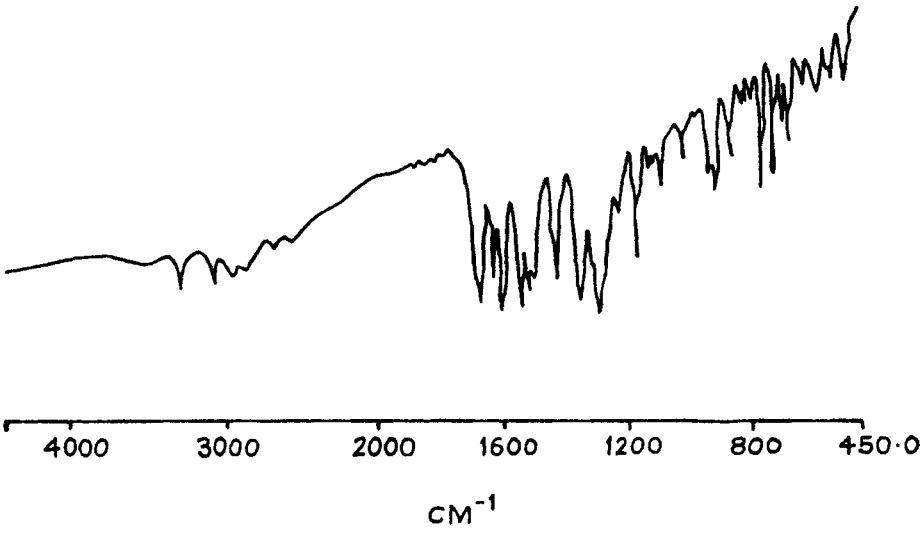

Figure 1

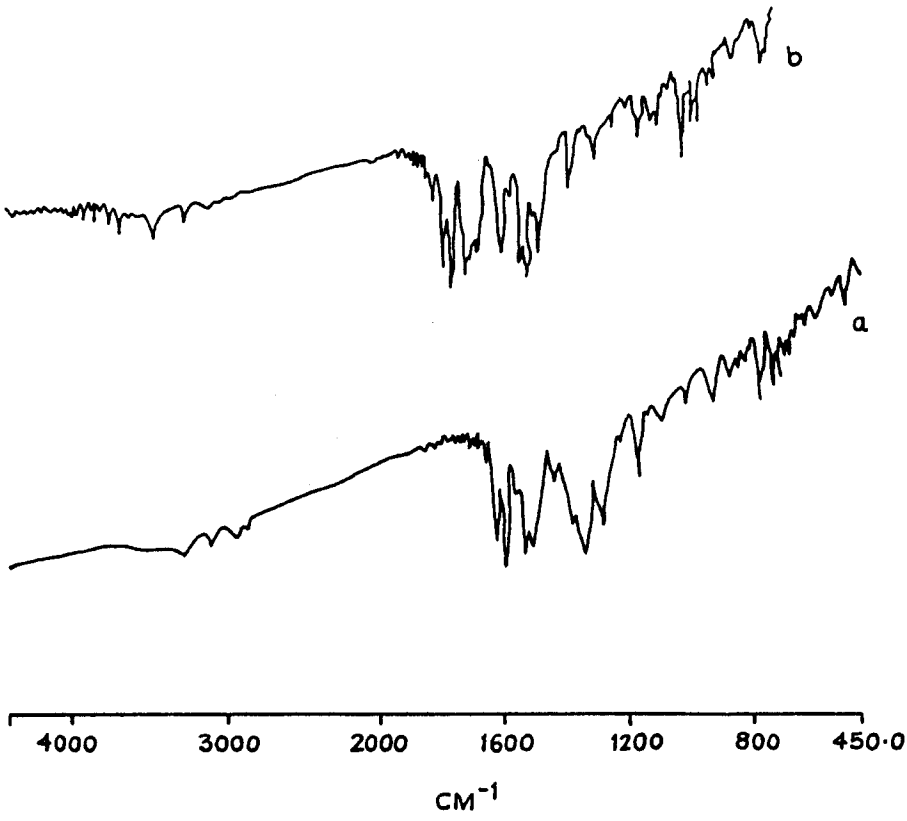

Figure 2

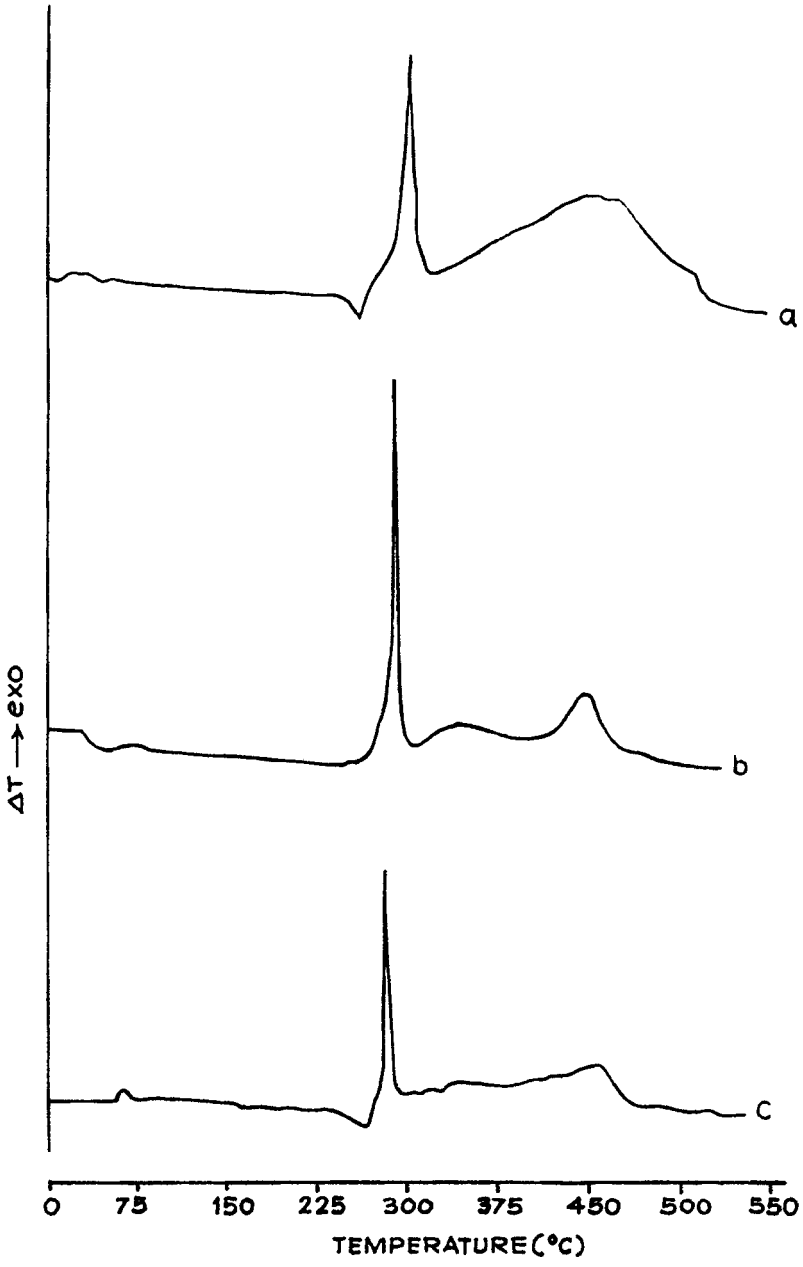

Figure 3