Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Transition metal salts of 2, 4, 6-trinitroanilinobenzoic acid - potential energetic ballistic modifiers for propellants

J. K. Nair[a]; M. B. Talawar[a]; T. Mukundan[a]
[a] High Energy Materials Research Laboratory, Pune

To cite this Article Nair, J. K. , Talawar, M. B. and Mukundan, T.(2001) 'Transition metal salts of 2, 4, 6-trinitroanilinobenzoic acid - potential energetic ballistic modifiers for propellants', Journal of Energetic Materials, 19: 2, 155 — 162
To link to this Article: DOI: 10.1080/07370650108216124
URL: http://dx.doi.org/10.1080/07370650108216124

TRANSITION METAL SALTS OF 2,4,6-TRINITROANILINOBENZOIC ACID - POTENTIAL ENERGETIC BALLISTIC MODIFIERS FOR PROPELLANTS

J.K. Nair, M.B. Talawar, and T. Mukundan

High Energy Materials Research Laboratory, Sutarwadi, Pune 411021

ABSTRACT

Iron (Fe^{2+} and Fe^{3+}), cobalt and nickel salts of 2,4,6-trinitroanilino benzoic acid have been synthesized, and characterized by elemental analysis, IR, metal content and explosive properties like impact and friction sensitivity. Differential thermal analysis shows the thermal stability of these salts as: ferrous, 270°C; ferric, 280°C; cobalt, 270°C; and nickel, 300°C. The impact sensitivity ($h_{50\%}$) of these salts are > 170 cm except for Fe^{3+}salt (156 cm). The friction sensitivity of all the salts were found to be > 36 kg. The salts were found to be devoid of any free acid present in them.

• Author for correspondence

Journal of Energetic Materials Vol. 19, 155-162 (2001)
Published in 2001 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

One of the important additives incorporated in a propellant mix is intended to modify the ballistic performance. Known as ballistic modifiers, these are generally metal salts of carboxylic acids. Basic lead salicylate, lead stearate etc. are such well known[1] examples. Salts of aromatic carboxylic acids are found effective as ballistic modifier in formulations that possess a high calorimetric value (cal val), while that of aliphatic carboxylic acids in low cal val formulations[2]. However, the carboxylic acid moiety in these salts are inert and does not contribute to the energetics. Carboxylic acids containing groups like nitro or azido could increase the total energy output. Metal salts of such acids are, therefore, energetic ballistic modifiers. The present study describes the synthesis and characterization of iron (Fe^{2+} and Fe^{3+}), cobalt and nickel salts of 2,4,6-trinitroanilinobenzoic acid, which is a nitro group containing acid synthesized from picryl chloride and *p*-aminobenzoic acid. To the best of our knowledge, this is the first report of the synthesis of transitional metal salts of an energetic carboxylic acid.

EXPERIMENTAL

Materials

Cobalt nitrate, nickel nitrate, ferrous sulphate, ferric nitrate, and sodium hydroxide used were of analytical grade obtained from Qualigens India Ltd. The solvents used were also of analytical grade.

Elemental Analysis was carried out on a Perkin Elmer elemental analyzer (Model No. 240). Infrared spectra were recorded at room temperature using KBr matrix in the region 4000-250 $cm,^{-1}$ using a Prekin Elmer infrared spectrophotometer model 683. Differential thermal analysis was carried out on a Netzsch thermal analyzer model 409 in static air. Alumina dried at 700 ^{0}C for one hour was used as reference material. Sample mass used was 10 mg and the rate of heating was 10 ^{0}C/min. Impact sensitivity was carried out on an impact sensitivity apparatus of fall hammer type with a falling weight of 2kg and friction sensitivity was measured using a Julius Peter friction sensitivity apparatus. Cobalt, nickel, ferrous and ferric content was estimated by gravimetric method [3].

2,4,6-Trinitroanilinobenzoic acid(TABA)was synthesized by the reported method[4] . New salts of TABA were synthesized as per Scheme 1

Synthesis

Preparation of cobalt salt of TABA

3.48g (0.01 mol) of TABA was added to an aqueous solution of 0.40g (0.01 mol) sodium hydroxide and warmed to 60^{0}C. To the aqueous sodium salt solution of TABA was added 0.91g (o.005 mol) of cobalt nitrate dissolved in 10 ml of water when a yellowish orange precipitate of cobalt salt of TABA separated out. The precipitate was filtered, washed with cold water, ethanol and dried at room temperature to obtain 6.25 g of the salt (Yield, 83%). Similarly Ni^{2+}, Fe^{3+} salts were prepared using corresponding metal nitrates where as the ferrous salt of TABA was prepared using ferrous sulphate.

RESULTS AND DISCUSSION

The experimentally obtained elemental analysis results are in good agreement with the calculated values. The percentage purity of the salts was found to be > 99% of theoretical. The gravimetrically observed percentage of metal content for cobalt, nickel and ferrous was 8% whereas for ferric salt it was 5%. The IR stretching frequencies of metal salts of TABA are presented in Table 1. The data confirm the expected structure of the metal salts, viz. $M^{2+}(C_{13}H_8N_4O_8)_2$ where $M^{2+} = Co^{2+}$, Ni^{2+}, or Fe^{2+} and $Fe^{3+}(C_{13}H_8N_4O_8)_3$

TABLE 1

IR stretching frequencies (cm^{-1}) of various salts

Salt	NH	CH	C=O	C=C	$C-NO_2$
Co^{2+}	3346	3078	1614	1600	1542 1344
Ni^{2+}	3328	3078	1614	1602	1540 1346
Fe^{2+}	3340	3112	1614	1600	1542 1346
Fe^{3+}	3282	3086	1626	1600	1540 1350

for ferric salt. The absence of stretching frequency around 3600 cm^{-1} due to -OH and the shifting of the characteristic carbonyl frequency[5] from 1670 cm^{-1} (in TABA) to 1614cm^{-1} (in salt) also corroborate the assigned structure of metal salts of TABA.

As evidenced by DTA curves, all salts decompose exothermically giving sharp exotherms characteristic of nitro compounds. The peak initiation temperature(T_i) and peak maxima(T_{max}) of the salts were: ferrous salt, 270 & 290; ferric, 280 & 360; cobalt, 270 & 300 and nickel, 300 & 308 °C. The thermal stability of these salts were thus found to be in the order ferric > nickel > cobalt > ferrous which is the expected order of thermal stability based on

the percentage of ionic character of the metal-oxygen bond in the sequence $O\text{-}Fe^{3+} > O\text{-}Ni^{2+} > O\text{-}Co^{2+} > O\text{-}Fe^{2+}$ as seen from electronegativities of the participating atoms. The T_i of ferric salt was found to be less than that of nickel which is an aberration from the theoretical sequence. The T_{max} of the salts, however, followed the expected order. The explosive properties namely impact and friction sensitivity data are presented in Table 2.

The results clearly indicate that these salts are insensitive to impact and friction. This result is in conformity with high thermal stability of these salts,

TABLE 2

Sensitivity data of the TABA salts

Compound name	Impact sensitivity (cm)	Friction sensitivity (kg)
Cobalt salt	> 170	> 36
Ferrous salt	> 170	> 36
Nickel salt	> 170	> 36
Ferric salt	156	> 36

because it is well known that the mechanism of initiation of explosives under impact is thermal in origin[6]. The salts were found to have no free acid in them as evidenced by the neutral *pH* of water washings.

CONCLUSION

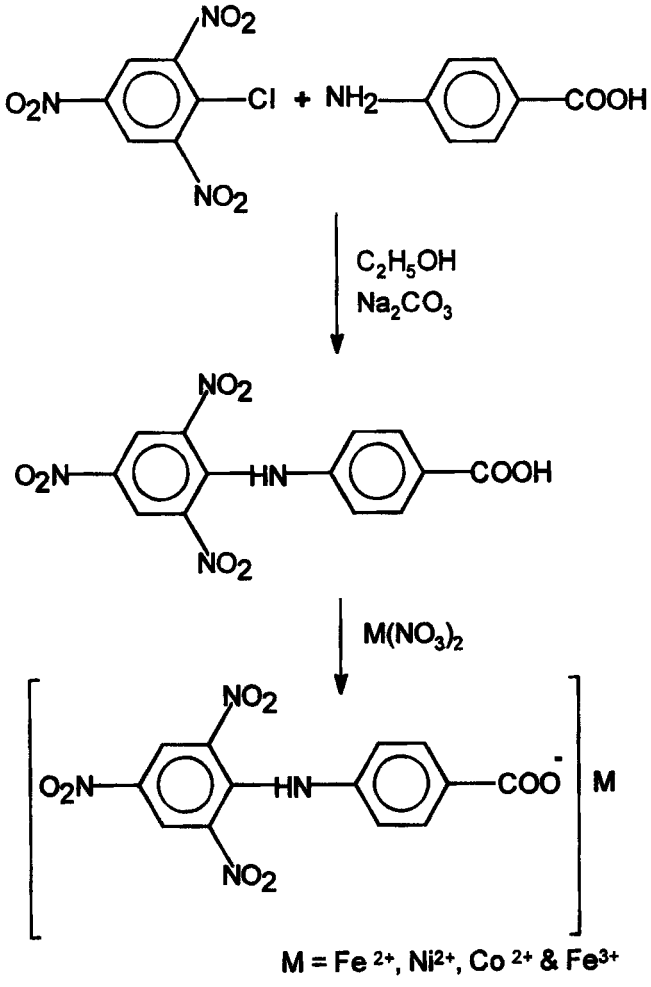
Ferrous, ferric, cobalt and nickel salts of 2,4,6-trinitroanilinobenzoic acid have been synthesized and characterized, as potential energetic ballistic modifiers. Out of these, cobalt and nickel salts are potential ballistic modifiers for use in double base propellant and iron salts in composite propellants.

ACKNOWLEDGEMENT

Authors thank Dr. Haridwar Singh, Director, HEMRL, Pune, for helpful discussion and permission to publish the results.

REFERENCES

1. Camp A T, US Patent No., 3,088,858 (1963)
2. Singh H and Rao K R K, AIAA Journal, 15, 1545 (1977)
3. Vogel A I, Text Book of Quantitative Inorganic analysis 4th Ed., (Longman, England) 1978
4. Wedekind E, Berichte Chemie, 33, 426 (1900)
5. Silverstein R M, Bassler C G, Morril T C, Spectrometric identification of Organic Compounds,(John Wiley & Sons Inc., London), 1991
6. Bowden F P and Yoffe A D, Initiation and growth of explosion in liquids and solids (Cambridge Univ. Press, London), 1952



SCHEME 1

Synthesis of metal salts of TABA