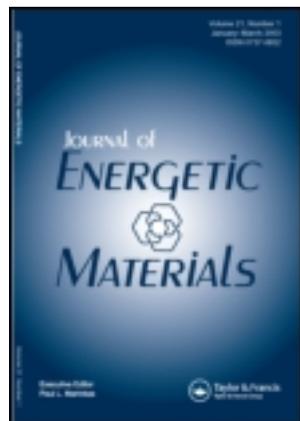


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Synthesis, Characterization, and Thermal and Explosive Properties of Alkali Metal Salts of 5,7-Diamino-4,6-Dinitrobenzofuroxan (CL-14)

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Synthesis, Characterization, and Thermal and Explosive Properties of Alkali Metal Salts of 5,7-Diamino- 4,6-Dinitrobenzofuroxan (CL-14)

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Potassium, rubidium, and cesium salts of 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) have been prepared by reacting sodium salt of 5,7-diamino-4,6-dinitrobenzofuroxan with alkali metal nitrate in an aqueous medium. The structure of the compounds was unequivocally confirmed by spectra data, elemental analyses, and estimation of metal content. Further, the compounds have been evaluated for explosive and thermal properties and found more suitable as compared to alkali metal salts of 4,6-dinitrobenzofuroxan (DNBF).

Keywords: characterization, synthesis, CL-14

Introduction

Heavy metal salts of certain weak acids such as hydrazoic, fulminic, picric, and styphnic acid have found extensive applications

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in military as well as civil sectors as initiatories/primary explosives [1, 2]. Similarly potassium salts of 4,6-dinitrobenzofuroxan (K-DNBF), being electron deficient in nature, form Meisenheimer complexes with electron-rich moieties [3, 4] and have been used in initiatory composition [5, 6]. These findings were further supported by our earlier publication [7] with alkali metal salts of DNBF.

It is believed that the replacement of nitro groups by furoxan groups can result in the increase of densities of explosive molecules and velocity of detonation, while the introduction of amino groups to the explosive molecules further enhances density and heat resistance, and the decrease of impact sensitivity [8, 9]. To utilize the advantage of furoxan and amino groups, 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) has been synthesized from DNBF [10], whose explosive properties are better than those of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). To exploit the advantages of amino groups in DNBF, we have synthesized some of the alkali metal salts of CL-14, which have not been reported in the literature.

In the following sections we report the synthesis, characterization, and thermal and explosive properties of four new alkali metal salts (Na, K, Rb, and Cs) of CL-14 and compare their properties with those of alkali metal salts (Na, K, Rb, and Cs) of DNBF.

Experimental

General Methods

The melting points were determined on open capillary tubes and are uncorrected. The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer using a KBr matrix. $^1\text{H-NMR}$ spectra were recorded on a Bruker 90 MHz instrument using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. Elemental analyses were performed on a Carlo-Erba elemental analyzer; EA 1108 and metal contents were determined by the "Ion Chromatography" model DIONEX 500, using cation column CS-12A with the eluent sulphuric acid and methane sulphonic acid.

Deflagration temperature [11] was determined by heating 0.02 g of the sample in a glass tube in Wood's metal bath at a

heating rate of 5°C/min. Differential thermal analysis was recorded by heating 2–3 mg of the sample at a heating rate of 10°C/min in the presence of static air. The impact sensitivity was determined by the Fall-Hammer method using 2 kg drop weight, and friction sensitivity was determined by using the Julius Peters apparatus by following standard methods [12]. A copper foil test was carried out by taking 10 mg of the sample in a copper foil; its decomposition pattern was observed by putting it over a direct flame.

Materials

4,6-Dinitrobenzofuroxan (DNBF, m.p. 173–74°C), prepared in the laboratory [7] from picric acid on treatment with pyridine followed by chlorination, azidation, and pyrolysis, was used as the starting material. Rubidium nitrate and cesium nitrate were procured from Aldrich Chemicals Co., while hydroxylamine hydrochloride, sodium hydrogen carbonate, and potassium nitrate were obtained from SQ Grade, Qualigens Fine Chemicals, and were used without further purification.

Synthesis

4,6-Dinitrobenzofuroxan (DNBF), 1. DNBF was synthesized by adopting our methods reported elsewhere [7], yielding 84%, m.p. 173–74°C, DTA 174°C (endotherm), and 273°C (exotherm).

IR (KBr) cm^{-1} : 3450 (hydrogen bonded –OH str.), 3106 (br-H str.), 1610 (C=C str.), 1590 and 1558 (furoxan ring str.), 1553 and 1334 (NO_2 asym. and sym. str.).

$^1\text{H-NMR}$ (DMSO- d_6 /TMS) δ ppm: 8.8 (s, 1H, C-5 aromatic proton), 8.94 (s, 1H, C-7 aromatic proton).

Anal. calcd. for $\text{C}_6\text{H}_2\text{N}_4\text{O}_6$ (mol. wt. 226): C 31.55; H 0.88; N 22.77. Found: C 31.59; H 0.60; N 24.46.

Sodium Salt of CL-14, 2. 4,6-Dinitrobenzofuroxan, **1** (5.0 g, 22.12 m mol), was transferred to a three-necked round-bottomed flask fitted with a stirrer, and distilled water (75 ml) was added to it. To the reaction mixture, sodium hydrogen carbonate (10.0 g, 119 m mol) and hydroxyl amine-hydrochloride (6.0 g

86.3 m mol) were added, and the mixture was stirred at 25°C for 3 hr. The reaction mixture was then cooled to 0°C, and the precooled 4 N sodium hydroxide solution (100 ml) was added to it. The resulting reaction mixture was further stirred for 3 hr at 25°C. The dark yellow product thus obtained was filtered and washed thoroughly with cold water till it became alkali free. It was then dried to yield 3.3 g (60%), m.p. 240°C (explodes with bang), DTA 242°C (exotherm with a big bang).

IR (KBr) cm^{-1} : 3348 and 3242 (NH_2 asym. and sym. str.) 1621, 1512, 1277, 1248 (furoxan ring), 1610 (C=C str.), 1545 and 1345 (NO_2 asym. and sym. str.) 1208 (C–N str.).

$^1\text{H-NMR}$ ($\text{DMSO-d}_6/\text{TMS}$) δ ppm: 10.2 (s, br, 2H, NH_2 C-5); 9.5 (s, br, 2H, NH_2 , C-7).

Anal. Calcd. for $\text{C}_6\text{H}_4\text{N}_6\text{O}_6\text{Na}$ (mol. wt. 279): C 25.80; H 1.43; N 30.10. Found: C 25.66; H 1.31; N 30.04.

Metal content (Na): Found 8.10% as against 8.24% (calcd.).

Potassium Salt of CL-14. To a 500 ml three-necked round-bottomed flask, sodium salt of CL-14, **2** (5 g, 17.92 m mol), was transferred carefully, and distilled water (250 ml) was added to it. The solution was warmed to 60°C to obtain a homogeneous solution. At this stage potassium nitrate (1.9 g, 18.8 m mol) dissolved in 25 ml of distilled water was added slowly to it. The reaction mixture was swirled and allowed to cool at ambient temperature and kept overnight. The yellow product thus obtained was filtered and washed 2–3 times with ice-cooled water and finally with diethyl ether. It was dried to yield 4.3 g (~81%), m.p. 265°C (explodes with bang). DTA 269°C (exotherm, with bang).

IR (KBr) cm^{-1} : 3346 and 3244 (NH_2 asym. and sym. str.), 1624, 1512, 1296, 1248 (furoxan ring), 1620 (C=C str.), 1546 and 1356 (NO_2 asym. and sym. str.), 1280 (C–N str.).

$^1\text{H-NMR}$ ($\text{DMSO-d}_6/\text{TMS}$) δ ppm: 10.2 (s, br, 2H, NH_2 , C-5) 9.5 (s, br, 2H, NH_2 , C-7).

Anal. calcd. for $\text{C}_6\text{H}_4\text{N}_6\text{O}_6\text{K}$ (mol. wt. 295): C 24.40; H 1.35; N 28.47. Found: C 24.16; H 1.19; N 28.28.

Metal content (K): Found 13.08% as against 12.22% (calcd.).

Rubidium Salt of CL-14. Sodium salt of CL-14, **2** (5 g, 17.92 m mol), was carefully transferred into a two-necked round-bottom flask, and distilled water (250 ml) was added to it. The flask, was warmed to 60°C to get a homogeneous solution. At this stage rubidium nitrate (2.8 g, 18.98 m mol) dissolved in 25 ml of distilled water was added slowly to it. The reaction mixture was swirled and allowed to attain an ambient temperature. The yellow precipitate obtained was filtered and washed 2–3 times with distilled water and dried to yield 5.2 g (85%), m.p. 281°C (explodes with big bang) DTA 285°C (exotherm with bang).

IR (KBr) cm^{-1} : 3352 and 3240 (NH_2 asym. and sym. str.), 1625, 1516, 1292, 1250 (furoxan ring), 1612 (C=C str.), 1554 and 1350 (NO_2 asym. and sym. str.), 1200 (C–N str.).

$^1\text{H-NMR}$ ($\text{DMSO-d}_6/\text{TMS}$) δ ppm: 10.24 (s, br, 2H, NH_2 , C-5) 9.48 (s, br, 2H, NH_2 , C-7).

Anal. calcd. for $\text{C}_6\text{H}_4\text{N}_6\text{O}_6$ Rb (mol. wt. 341.5): C 21.08; H 1.17; N 24.59. Found: C 20.92; H 0.90; N 24.36.

Metal content (Rb): Calcd. 25.03% and found 24.95%.

Cesium Salt of CL-14. To a 500 ml three-necked round-bottom flask, sodium salt of CL-14, **2** (5 g, 17.92 m mol), was transferred, and distilled water (250 ml) was added to it. the solution thus obtained was warmed to 60°C to get a homogeneous solution. At this stage cesium nitrate (3.8 g, 19.49 m mol) dissolved in 25 ml of distilled water was added and swirled 2–3 times. The solution was cooled to ambient temperature. The light yellow precipitate obtained was filtered and washed thoroughly with cold water. It was dried and afforded a yield of 5.8 g (~83%), m.p. 277°C (explodes with bang), DTA 280°C (exotherm with bang).

IR (KBr) cm^{-1} : 3356 and 3248 (NH_2 asym. and sym. str.), 1625, 1510, 1295, 1248 (furoxan ring), 1608 (C=C str.), 1546 and 1354 (NO_2 asym. and sym. str.), 1205 (C–N str.).

$^1\text{H-NMR}$ ($\text{DMSO-d}_6/\text{TMS}$) δ ppm: 10.22 (s, br, 2H, NH_2 , C-5), 9.52 (s, br, 2H, NH_2 , C-7).

Anal. Calcd. for $\text{C}_6\text{H}_4\text{N}_6\text{O}_6\text{Cs}$ (mol. wt. 388.9): C 18.51; H 1.02; N 21.59. Found: C 18.32; H 0.79; N 21.44.

Metal content (Cs): 34.46% as against 34.17% (calcd.).

Results and Discussion

4,6-Dinitrobenzofuroxan, **1**, the starting material for the synthesis of sodium, potassium, rubidium, and cesium salts of 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14), was prepared by following the reaction scheme depicted in Figure 1.

Picric acid on treatment with pyridine followed by chlorination in the presence of phosphorus oxychloride yielded picryl chloride, which on azidation followed by pyrolysis produces compound **1**. Compound **1** thus obtained was aminated through "vicarious nucleophilic substitution," in the presence of hydroxylamine hydrochloride and sodium bicarbonate, resulting in the formation of sodium salt of CL-14, compound **2**. Compound **2** was further treated with potassium nitrate, rubidium nitrate, cesium nitrate,

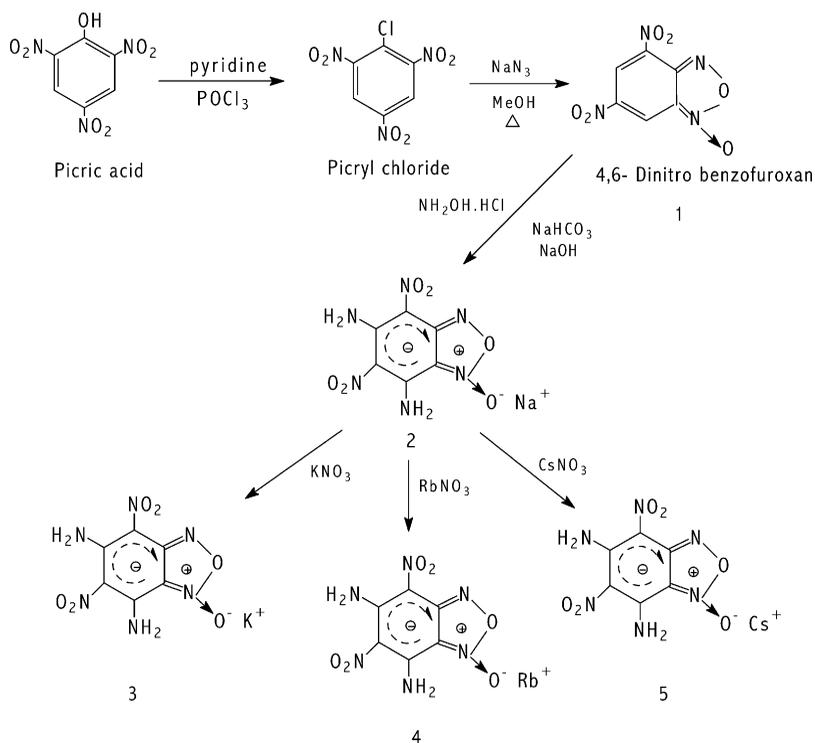


Figure 1. Synthetic route for alkali metal salts of CL-14.

and cesium nitrate to obtain corresponding alkali metal salts of CL-14 with an excellent yield and purity.

Sodium salt of CL-14 could not be prepared following the identical procedure as reported for sodium salt of 4,6-dinitrobenzofuroxan [6]. Therefore, a significant amount of efforts had been directed to chalk out the strategy for the synthesis of sodium salt of CL-14, the precursor for other alkali metal salts. The detailed procedure for the same is given above in the section entitled "Synthesis." Compounds **2**, **3**, **4**, and **5** are dark yellow– to canary yellow–colored solids with melting points 240°C (dec), 265°C (dec), 281°C (dec), and 277°C (dec), respectively. All compounds have been characterized satisfactorily by spectral data, elemental analysis, and percent estimation of metal content. The infrared spectra of the four salts are of similar nature, suggesting that all compounds possess general characteristics of structural features. The IR spectra of the compounds in general show strong absorption bands at 3354 and 3244 cm^{-1} for $-\text{NH}_2$ asymmetric and symmetric stretching frequencies, and 1625, 1510, 1295, 1248 stretching frequencies are due to the furoxan ring. The $-\text{C}=\text{C}$ and $-\text{C}-\text{N}$ stretching frequencies appear at 1612 and 1208 cm^{-1} , while the asymmetric and symmetric stretching vibration of $-\text{NO}_2$ groups appear at 1550–1546 and 1354–1340 cm^{-1} , respectively. In $^1\text{H-NMR}$, NH_2 protons at C-5 in the aromatic ring resonate at δ 10.2, while the chemical shift of $-\text{NH}_2$ protons at C-7 appears at a higher field, around δ 9.5. The elemental analysis data and metal contents of compounds **2**, **3**, **4**, and **5** are in excellent agreement with the calculated values, which further confirms the purity of the compounds.

Compounds **2**, **3**, **4**, and **5** were also evaluated for thermal and explosive properties; the data obtained are presented in Table 1. Compounds **2**, **3**, **4**, and **5** deflagrate at 242°C, 264°C, 286°C, and 278°C, which was further supported by the DTA exotherms 242°C, 269°C, 285°C, and 280°C, respectively. Thus, it is evident from the results that thermal stability of compounds **2**, **3**, **4**, and **5** has increased drastically by introduction of amino groups in the 4,6-dinitrobenzofuroxan ring at C-5 and C-7 positions as compared with the Na, K, Rb, and Cs salts of

Table 1
Comparative data on thermal and explosive properties of alkali metal salts of CL-14 and DNBF

Properties	Na CL-14	K CL-14	Rb CL-14	Cs CL-14	Na-DNBF	K-DNBF	Rb-DNBF	Cs-DNBF
Melting point, °C	240 (explodes with bang)	265 (explodes with bang)	281 (explodes with bang)	277 (explodes with bang)	161–162 (explodes)	215 (explodes)	188.89 (explodes)	165.66 (explodes)
Deflagration, °C	242 (bang)	264 (bang)	286 (bang)	278 (bang)	160 (bang)	220 (explodes)	188 (explodes)	166 (explodes)
DTA (Exo), °C	242 (bang)	269 (bang)	285 (bang)	280 (bang)	163	222	188	165
Impact sensitivity (heat of 50% explosion), cm ^a	75	65	50	42	33.5	35.0	35.0	30.0
Friction sensitivity (insensitive up to), kg ^b	36	32.4	28.8	16.0	5.4	3.8	1.0	0.2

^aSensitivity to impact: RDX, 35 cm; TNT, 110 cm; tetryl, 85 cm.

^bSensitivity to friction: RDX, 12 kg; TNT, 32.4 kg; tetryl, 32.4 kg.

DNBF[7]. The increase in thermal stability of compounds **2**, **3**, **4**, and **5** may be attributed to intra- and intermolecular hydrogen bondings.

The study of explosive properties (Table 1) reveals that compounds **2**, **3**, **4**, and **5** are safe toward impact, and a sensitivity trend was obtained in the order $\mathbf{2} < \mathbf{3} < \mathbf{4} < \mathbf{5}$. The friction sensitivity data (Table 1) also reveal that these compounds are safe toward friction, while the same sensitivity trend was observed as in the case of impact sensitivity. Thus, compound **5** is the most sensitive in the series.

To explore their suitability in electro explosive devices (EED) as fuel, a copper foil test was carried out. The main objective of this test is to explore the utility of molecules in EED systems. During this test, when a compound burns with flame along with a bang, it may be used in the system as a fuel. Our preliminary investigation indicates that sodium and potassium salts of CL-14 did not give any flame or sound, while rubidium salt gives a low crackling sound along with a small flame. However, cesium salt of CL-14 gives a very good flame along with a bang.

Conclusion

Sodium, potassium, rubidium, and cesium salts of CL-14 have been successfully synthesized and characterized. The preliminary data on these salts reveal that their thermal stability is better than that of alkali metal salts of DNBF.

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