



Synthesis, Characterization and Single Crystal Structure of Carbanionic Sigma Complexes of Sodium and Potassium Salts

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ABSTRACT

Barbituric acid derivatives are very much effective in anxiolytics, hypnotics and anticonvulsant agents. In this context in the present investigation, new molecular salts have been synthesized in the crystalline form. They have been characterized through UV-Vis, IR, ¹H NMR, ¹³C NMR, and X-ray diffraction studies. In this anion, 1,3-dimethylbarbituric acid ring and substituted dinitrophenyl ring, linked via a C-C bond.

Keywords: Sodium methoxide, Potassium methoxide, UV, FT-IR, H NMR, X-ray diffraction.

INTRODUCTION

Synthetic nitroaromatic compounds widely used in a variety of materials, including drugs¹⁻³, pharmaceutical dyes⁴⁻⁵, explosives⁶⁻⁷, plastics, and pesticides. Several high energy density molecules are derived from nitroaromatic compounds⁸⁻¹⁰. Nitroaromatic compounds are electron-deficient and react readily with electron-rich species. With electron-rich organic and inorganic bases, they undergo many types of reactions¹¹⁻¹⁴. Depends on the nature of electron-deficient nitroaromatic compounds and electron-rich species, they had three different types of interactions which occur, leading to the formation of Charge transfer complexes¹⁵, Radical anion¹⁶ and Anionic sigma complexes¹⁷.

2, 4-Dinitrochlorobenzene (1-chloro-2, 4-dinitrobenzene) is a unique functional group used in medicinal chemistry. Nitro group is associated with mutagenicity and genotoxicity and therefore is often used in the drug discovery process¹⁸. The nitroaromatic compound is also used to synthesize dyes and high energy materials. These compounds are very common environmental pollutants that are used as pesticides and explosives¹⁹. DNCB molecule used in the preparation of many diverse organic molecules and biologically active molecules in recent years.

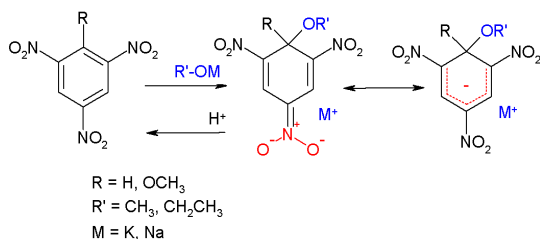
Barbituric acid (1,3-barbituric acid) has an active methylene group, i.e., (a cyclic molecule). It is expected to form a carbanion in the presence of a base. The C-5hydrogen atom substitution gives the



complexes. Dyes involving active methylene group of barbituric acid have been considered in recent years^{20,21,22,23}.

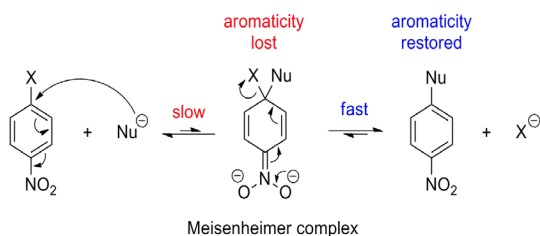
Mechanism

Strong interaction between the base and the aromatic compound results in sigma adduct formation²⁴. A particular transfer of electronic charge from the base to the aromatic nucleus depleted of π electron density gives rise to the π -complex known as donor-acceptor or charge-transfer complex²⁵. The complete transfer of an electron from the base to the nitroaromatic compound results in the formation of radical anion²⁶. If the nitroaromatic bears a substituted alkyl group, carbanion is formed due to proton abstraction²⁷. The mechanism is given in scheme 1.



Scheme 1

Most of these reactions have been made many reviews written²⁸⁻³⁴. Several reactions can proceed through cyclohexadiene ion of finite stability³⁵⁻³⁷. As aromaticity is disrupted during the formation of the sigma complex, considerable changes occur in electronic configuration and hence visible spectroscopy has been a primary tool in deducing complex-forming reactions³⁸⁻⁴⁰. The following mechanism is shown in Scheme 2.



Scheme 2

The carbanionic sigma complex can also be made as sensors in many fields such as industry, environment, and biotechnology.

EXPERIMENTAL METHODS

Synthesis of molecular salts

1-Chloro 2,4-dinitrobenzene (DNCB)

is dissolved in 30 mL of ethanol be mixed with 1,3-dimethyl barbituric acid in 30 mL of ethanol. Then added Sodium/potassium methoxide in 30 mL of ethanol and shaken for 2-3 hours. The excess ethanol be removed by distillation also the remaining solution was kept for one week when red colored crystals separated. These crystals recrystallized from distilled ethanol.

Thin Layer Chromatographic studies

The study was carried out to check the purity of the isolated molecules. Silica gel was used as an adsorbent. The slurry of silica gel was made with chloroform and coated uniformly on a TLC plate. The complex solution was prepared in pure absolute ethanol and spotted on the plate. The eluent used was the mixture of tertiary butyl alcohol and ethyl acetate.

RESULTS AND DISCUSSION

In the present investigation, a red crystalline solid is obtained and the yield is 42% and 75%.

Crystal structure determination of complexes

Crystal structure of sodium salt

The amorphous solid of sodium salt is crystallized from ethylene glycol. The sodium cations are bridged through an oxygen atom of 1-chloro-2,4-dinitro benzene and 1,3-dimethyl barbituric acid. In barbiturate residue bond lengths, bond angles are well-matched with that of barbiturate ion⁴² and it shows the delocalization of negative charge. The crystal data represent selected bond angles, bond distances of sodium salt. According to X-ray crystallographic data, the isolated molecule is monoclinic system. The unit cell parameters having P121/n1 space group $a=7.3269(5)$ Å, $b=19.9241(13)$ Å, $c=11.5431(9)$ Å, $V=1665.1(2)$ Å³; $Z=4$.

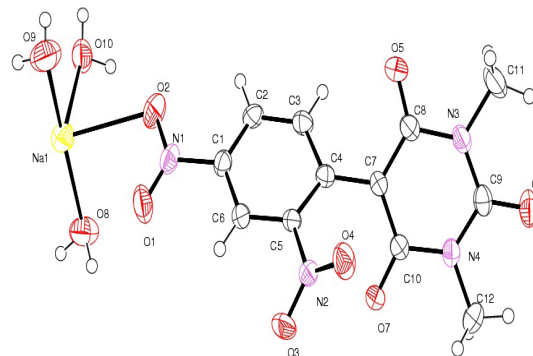


Fig. 1. ORTEP View of sodium Complex

Crystal structure of potassium salt

The structure of the potassium complex with DNCB, the crystals have been confirmed based on unit-cell contents. The crystal studies indicate that potassium cations are 8-coordinated and are bridged by an oxygen atom of 1,3-dimethyl barbituric acid. The K-O bond length range is 2.778-3.8699 (Shrivastava & Speakman, 1961). The Single-crystal XRD results have shown that the potassium salt of the present investigation possesses organometallic polymeric association. The crystal data represent selected bond distances, bond angles of potassium salt. The molecule is monoclinic crystal system having P21/n space group and cell parameters are a=11.3166(7) Å, b=7.2477 Å, c=20.3511(11) Å; Z=4.

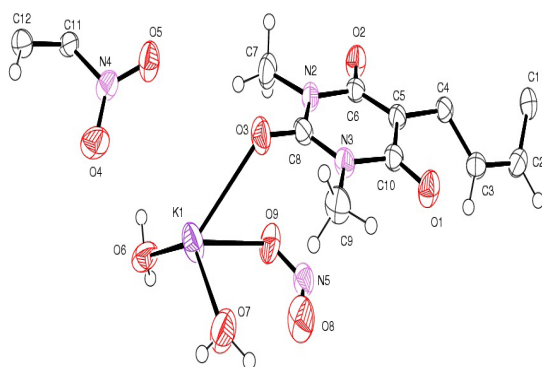


Fig. 1a. ORTEP View of potassium Complex

UV-Visible Analysis

In the UV-Vis spectrum, the two peaks are formed with λ_{max} values of 287.30nm, 484.34nm, and 245.93 nm, 446.86 nm (Figure 2, 2a).

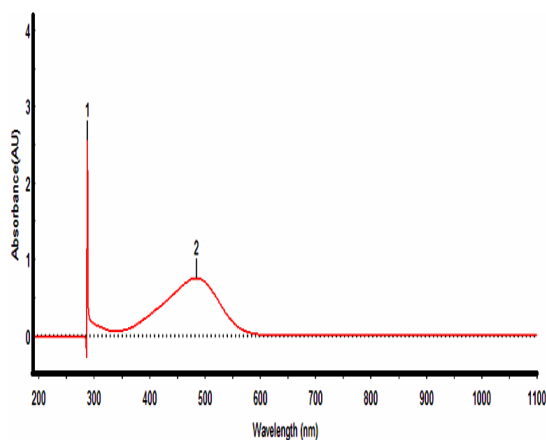


Fig. 2. UV-Visible Spectrum of sodium Complex

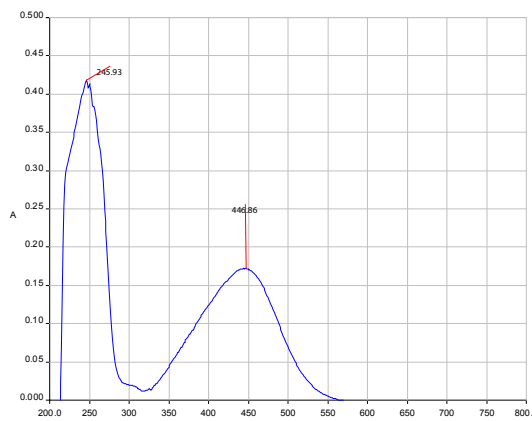


Fig. 2a. UV-Visible Spectrum of potassium Complex

FT-IR Analysis

FT-IR spectra are shown in (Fig. 3, 3a). NO₂ asymmetric and symmetric stretching frequency is 1536 cm⁻¹, 1532 cm⁻¹ and 1331 cm⁻¹, 1327 cm⁻¹. Here, C-Cl band is absent in the synthesized molecule The broad band observed between ~3600-2100 cm⁻¹ is characteristic of amine salt [43]. Carbonyl stretching frequency of 1,3-diethyl barbituric acid 1680 cm⁻¹ and 1670 cm⁻¹ during the formation of the complex.

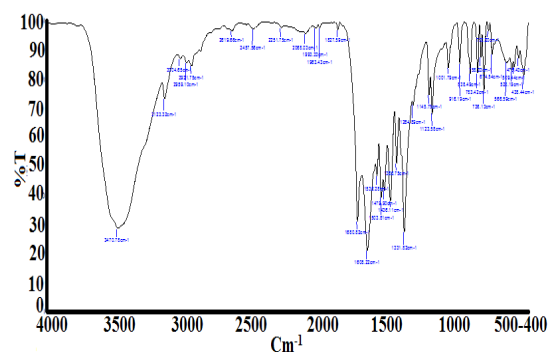


Fig. 3. FT-IR Spectrum of sodium Complex

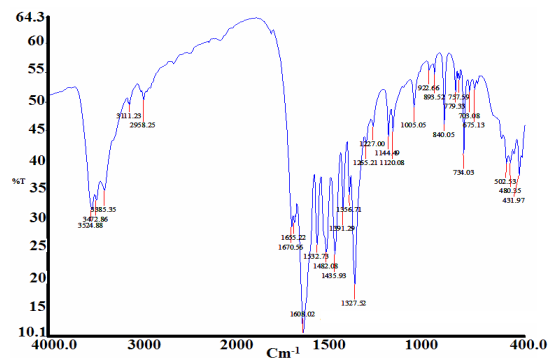


Fig. 3a. FT-IR Spectrum of Potassium Complex

NMR Analysis

¹H NMR spectra are depicted in (Fig. 4, 4a). This shows two peaks characteristics of the ring protons, one at δ 8.1 ppm (S, 2H) and another at δ 8.3 ppm (S, 1H) are observed. The peak corresponding to six methyl protons appears at δ 3.1 ppm. ¹³C NMR spectra of molecular salts are presented in (Fig. 5, 5a). ¹³C NMR spectrum indicate ten different carbon environments in the molecule. The peaks at 141.5 ppm and 87.1 ppm represents formation of C=C.

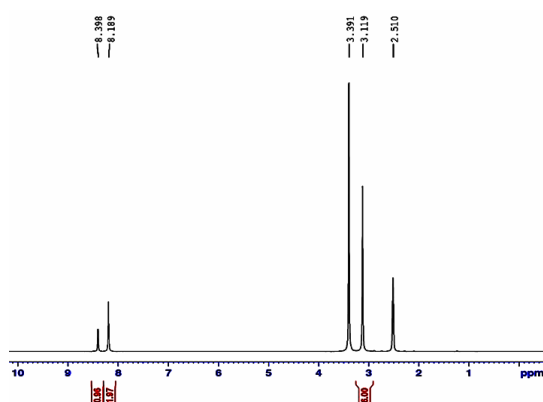


Fig. 4. ¹H-NMR Spectrum of Sodium Complex

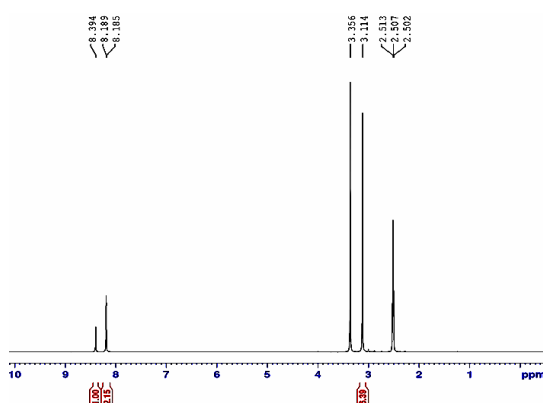


Fig. 4a. ¹H-NMR Spectrum of Potassium Complex

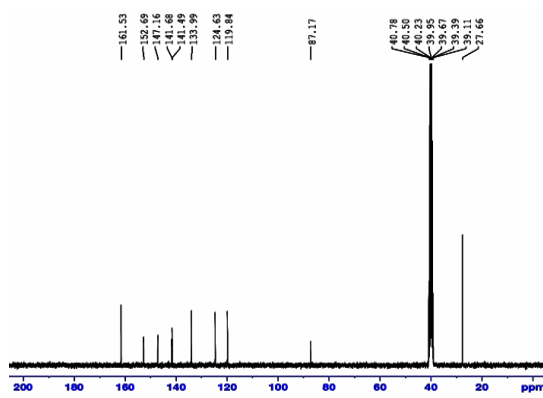


Fig. 5. ¹³C NMR Spectrum of Sodium Complex

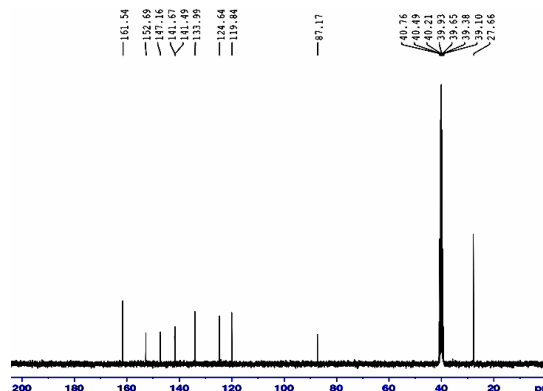


Fig. 5a. ¹³C NMR Spectrum of potassium complex

Table 1: Bond angles (°)

O8-Na1-O9	163.11(17)	O8-Na1-O10	83.38(15)
O9-Na1-O10	107.24(18)	O8-Na1-O10	105.47(16)
O9-Na1-O10	89.58(17)	O10-Na1-O10	79.92(13)
O8-Na1-O2	92.73(14)	O9-Na1-O2	82.65(17)
O10-Na1-O2	156.10(15)	O10-Na1-O2	78.44(12)
O8-Na1-O3	90.31(13)	O9-Na1-O3	75.29(15)
O10-Na1-O3	99.05(12)	O10-Na1-O3	163.88(16)
O2-Na1-O3	104.56(12)	O8-Na1-O1	70.05(13)
O9-Na1-O1	95.85(16)	O10-Na1-O1	149.52(13)
O10-Na1-O1	120.71(12)	O2-Na1-O1	44.35(9)
O3-Na1-O1	67.40(10)	O8-Na1-Na1	95.74(12)
O9-Na1-Na1	100.81(14)	O10-Na1-Na1	40.17(9)
O10-Na1-Na1	39.75(8)	O2-Na1-Na1	117.54(11)
O3-Na1-Na1	137.02(11)	O1-Na1-Na1	153.42(12)
O8-Na1-H6O	160.(3)	O9-Na1-H6O	22.(4)
O10-Na1-H6O	85.(4)	O10-Na1-H6O	88.(3)
O2-Na1-H6O	104.(3)	O3-Na1-H6O	76.(3)
O1-Na1-H6O	116.(4)	Na1-Na1-H6O	86.(4)
N1-O1-Na1	87.9(2)	N1-O2-Na1	104.5(3)
N2-O3-Na1	127.3(3)	Na1-O8-H2O	117.(4)
Na1-O8-H1O	116.(5)	H2O-O8-H1O	89.(6)
Na1-O9-H5O	139.(7)	Na1-O9-H6O	73.(10)
H5O-O9-H6O	100.(10)	Na1-O10-Na1	100.08(13)
Na1-O10-H3O	122.(6)	Na1-O10-H3O	104.(5)
Na1-O10-H4O	107.(5)	Na1-O10-H4O	115.(5)
H3O-O10-H4O	109.(7)		

Table 1a: Bond angles (°)

C12-C1-C2	121.66(17)	C12-C1-N5	118.92(1)
O1-C10-N3	117.05(16)	C5-C10-N3	116.22(16)
C12-C11-C4	123.45(17)	C12-C11-N4	114.88(16)
C4-C11-N4	121.54(16)	C1-C12-C11	118.11(17)
O7-K1-O3	94.57(7)	O7-K1-O6	137.71(7)
O3-K1-O6	125.02(6)	O6-K1-O6	92.26(6)
O7-K1-O4	74.48(7)	O3-K1-O4	159.63(5)
O6-K1-O4	63.28(5)	O6-K1-O4	69.12(6)
O7-K1-O9	109.66(6)	O3-K1-O9	71.94(5)
O6-K1-O9	73.87(5)	O6-K1-O9	162.89(6)
O4-K1-O9	95.25(5)	O7-K1-O4	129.72(6)
O3-K1-O4	97.47(5)	O6-K1-O4	65.55(5)
O6-K1-O4	59.45(5)	O4-K1-O4	102.74(4)

O9-K1-O4	120.50(5)	O7-K1-O8	70.96(6)
O3-K1-O8	78.03(5)	O6-K1-O8	100.18(6)
O6-K1-O8	139.20(5)	O4-K1-O8	82.13(5)
O9-K1-O8	38.83(5)	O4-K1-O8	159.31(5)
O7-K1-K1	109.17(6)	O3-K1-K1	145.66(4)
O6-K1-K1	46.42(4)	O6-K1-K1	45.83(4)
O4-K1-K1	54.47(4)	O9-K1-K1	119.57(5)
O4-K1-K1	48.27(3)	O8-K1-K1	132.51(5)
O7-K1-H2O	12.6(7)	O3-K1-H2O	105.8(7)
O6-K1-H2O	128.5(7)	O6-K1-H2O	62.8(7)
O4-K1-H2O	65.7(7)	O9-K1-H2O	118.2(7)
O4-K1-H2O	121.0(7)	O8-K1-H2O	79.5(7)
K1-K1-H2O	96.6(7)	C8-N2-C6	123.46(16)
C8-N2-C7	117.88(16)	C6-N2-C7	118.55(16)
C8-N3-C10	124.37(15)	C8-N3-C9	117.53(16)
C10-N3-C9	118.10(16)	O5-N4-O4	123.19(18)
O5-N4-C11	118.60(16)	O4-N4-C11	118.15(17)
C8-O3-K1	126.35(14)	N4-O4-K1	145.39(15)
N4-O4-K1	111.01(13)	K1-O4-K1	77.26(4)
K1-O6-K1	87.74(6)	K1-O6-H4O	107.(2)
K1-O6-H3O	105.(2)	K1-O6-H3O	134.(3)
K1-O7-H1O	118.(3)	H4O-O6-H3O	101.(3)
H1O-O7-H2O	131.(2)	K1-O7-H2O	109.(3)
N5-O9-K1	102.(4)	N5-O8-K1	90.75(13)
O8-N5-C1	106.82(14)	O8-N5-O9	122.32(18)
	119.45(19)	O9-N5-C1	118.23(19)

Table 2: Bond Lengths

C8-O5	C8-O5	C8-O5	C8-O5
1.241(5)	1.241(5)	1.241(5)	1.241(5)
C8-N3	C8-N3	C8-N3	C8-N3
1.415(5)	1.415(5)	1.415(5)	1.415(5)
C9-N3	C9-N3	C9-N3	C9-N3
1.368(6)	1.368(6)	1.368(6)	1.368(6)
C9-N4	C9-N4	C9-N4	C9-N4
1.377(5)	1.377(5)	1.377(5)	1.377(5)
C10-O7	C10-O7	C10-O7	C10-O7
1.248(4)	1.248(4)	1.248(4)	1.248(4)
C10-N4	C10-N4	C10-N4	C10-N4
1.400(5)	1.400(5)	1.400(5)	1.400(5)
C11-H11A	C11-H11A	C11-H11A	C11-H11A
0.96	0.96	0.96	0.96
C11-H11B	C11-H11B	C11-H11B	C11-H11B
0.96	0.96	0.96	0.96
C11-H11C	C11-H11C	C11-H11C	C11-H11C
0.96	0.96	0.96	0.96

Table 2a: Bond Lengths

K1-O3	2.7228(16)	K1-O6	2.778(2)
K1-O6	2.8058(18)	K1-O4	2.9608(19)
K1-O9	3.0265(18)	K1-O4	3.2287(17)
K1-O8	3.3488(19)	K1-K1	3.8699(10)

CONCLUSION

The present study focused on the characterization through various studies of carbanionic sigma complexes. Spectral data are inconsistent with the putative structure and further evidenced by single crystal XRD data. Various types of interactions possible between electron deficient compounds nitro aromatic compounds and bases are described. The cation and anion moiety are connected by hydrogen bonds. The complex for this work is stable in nanosize. Therefore, these may be changed into a potent drug in future.

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Conflict of Interest

The authors declare no conflict of interest.

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