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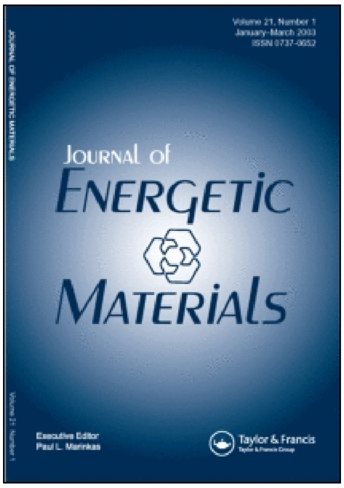

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# Preparation and characterisation of nitrophenates of transition metals

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# PREPARATION AND CHARACTERISATION OF NITROPHENATES OF TRANSITION METALS

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## ABSTRACT

A large number of nitrophenates of transition metals have been prepared and characterised during the programme of formulation of new energetic materials. These compounds have been found to be ionic salts having variable number of water of crystallisation.

## INTRODUCTION

Interest in the systematic preparation and characterisation of nitrophenates of transition metals thrives due to the fact that these compounds find application in explosive compositions.[1-5] Because of the presence of both fuel and oxidizer groups along with the metal ion (catalyst), in the same molecule, these are expected to be good candidates for propellant formulations. Although, picrates of many metals are known but their structure is still debated.

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Agrawal et.al.[4,5] reported that the nitrophenates are partially ionic and the thermal stability increases with the increase in the number of nitro groups, due to the increase in ionic character of oxygen-metal polar bond. Silberrad[2] reported that metal picrates are purely ionic compounds, with variable number of crystallisation. Further, it has also been reported[6] that highly hydrated compounds are less sensitive to heat, shock, friction and impact whereas, anhydrous are the more sensitive ones. However, work on the preparation and characterisation of these compounds is quite meagre.

In our programme of preparing new energetic matetials,[1,7-9] it was decided to prepare various nitrophenates of 3d transition metal series. Gravimetric estimation, Karl-Fischer titration, conductivity and UV spectral studies were undertaken in order to characterise these compounds. CAUTION! These compounds are highly explosives, hence other spectroscopic (IR, NMR, MS) and C,H,N analyses are out of our reach. The results show that all these compounds are purely ionic. Their behaviour towards heat, impact and friction has also been carried out, which .would be submitted elsewhere.

## EXPERIMENTAL

### Materials

Picric acid (BDH) and 2,4-dinitrophenol (Thomas Baker) were

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used as received without any further purification. 2-nitrophenol (BDH) was recrystallised from hot water, whenever required. Carbonates of nickel (Thomas Baker), zinc (Sarabhai), ferrous (Loba), cobalt, copper (BDH) and manganese acetate (Sarabhai) were used as such.

Methods of Preparation of Nitrophenates of Transition Metals.

Generally, nitrophenates are prepared by interacting transition metal cation with mono-, di- or tri-nitrophenol.[1-5] We have prepared the nitrophenates of manganese, ferrous, cobalt, nickel, copper and zinc by reacting suspension of corresponding nitrophenol in boiling water with freshly prepared hydroxide of these metals as given in the Scheme.

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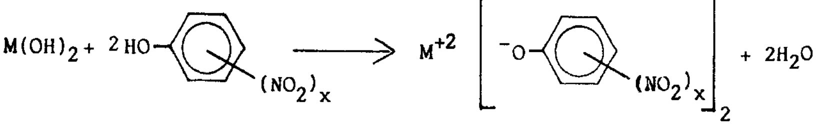
Scheme



**Where x = 1, 2 or 3 and M = Mn, Fe, Co, Ni, Cu or Zn.**

Metal hydroxides were prepared by treating sodium hydroxide with carbonate or acetate of the above metals. In case of trinitrophenates (TNP), crystalline solids were obtained on cooling the reaction mixture in ice bath. The mono- and dinitrophenates (MNP and DNP) were recovered on concentrating the respective solution with rotary vaccum evoporator (JSGW) at low temperature (60 °C) and pressure (200 mm Hg). All the compounds were recrystallised in hot water and their purity were checked by thin layer chromatography (TLC). These compounds have different colours, which are reported in the Table. It may be noted that their colour may be due to the presence of chromophoric($-NO_2$) group(s). It seems that unpaired electrons in the metal ions and presence of water molecule do not play any role for the colour of the compounds. The melting points could not be determined, because they start decomposing prior to melting. However, melting was observed just prior to explosion, in all the cases. The percentage of each metal was estimated gravimetrically. The formation of corresponding metal oxides was also confirmed by heating the samples of MNP, DNP and TNP with $Al_2O_3$ (1:4 ratio) at a slow heating rate upto 600 °C. $Al_2O_3$ was added as diluent to avoid detonation.

## Conductivity Measurements on Nitrophenates of Transition Metals and Nitrophenols.

The conductivity of these nitrophenate salts and nitrophenols was measured in micro mhos $cm^{-1}$ at 0.005 M concentration and at 25 °C by using digital conductivity meter (Chemito) with a conductivity cell having cell constant of 0.748. The solutions were prepared in conductivity water and the conductance data are reported in the Table.

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**Table** Molecular Formula, Water of Crystallisation, Molecular Weight, Colour, Percentage of Metal, Conductance and UV Absorbtion Data of Nitrophenates of Transition Metals and Nitrophenols.

| Molecular Formula | Water of Crystal-lisation | Mol.Wt. | Colour | % of Metal |  | Conduc-tance $\mu\Omega^{-1}cm^{-1}$ | $\lambda_{max}$/nm |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Ther. | Exp. |  | I band | II band | III band |
| Mn $[(NO_2)C_6H_4O]_2$ | 0 | 331.14 | Deep orange | 16.59 | 15.60 | 9.1 | 210 | 278 | 351 |
| Mn $[(NO_2)_2C_6H_3O]_2$ | 2 | 457.17 | Golden yellow | 12.02 | 11.82 | 8.7 | 222 | 256 | 360 |
| Mn $[(NO_2)_3C_6H_2O]_2$ | 2 | 547.16 | Deep yellow | 10.04 | 9.91 | 6.2 | 205 | 238 | 356 |
| Fe $[(NO_2)C_6H_4O]_2$ | 0 | 332.05 | Deep orange | 16.82 | 17.72 | 10.4 | 209 | 279 | 351 |
| Fe $[(NO_2)_2C_6H_3O]_2$ | 2 | 458.07 | Lemon yellow | 12.19 | 11.75 | 8.1 | 223 | 257 | 360 |
| Fe $[(NO_2)_3C_6H_2O]_2$ | 2 | 548.07 | Deep yellow | 10.19 | 9.48 | 6.2 | 207 | 237 | 356 |
| Co $[(NO_2)C_6H_4O]_2$ | 1 | 353.15 | Deep red | 16.69 | 16.32 | 11.1 | 209 | 279 | 351 |
| Co $[(NO_2)_2C_6H_3O]_2$ | 3 | 479.18 | Brick red | 12.30 | 11.26 | 7.2 | 220 | 257 | 360 |
| Co $[(NO_2)_3C_6H_2O]_2$ | 4 | 587.18 | Parrot green | 10.03 | 9.35 | 5.7 | 205 | 237 | 356 |
| Ni $[(NO_2)C_6H_4O]_2$ | 0 | 334.89 | Deep red | 17.57 | 17.58 | 10.3 | 210 | 279 | 351 |
| Ni $[(NO_2)_2C_6H_3O]_2$ | 2 | 460.92 | Lemon yellow | 12.73 | 12.63 | 9.6 | 220 | 257 | 360 |
| Ni $[(NO_2)_3C_6H_2O]_2$ | 5 | 604.96 | Deep yellow | 9.70 | 9.48 | 5.8 | 205 | 238 | 356 |
| Cu $[(NO_2)C_6H_4O]_2$ | 0 | 339.75 | Deep orange | 18.70 | 19.46 | 9.6 | 210 | 279 | 351 |
| Cu $[(NO_2)_2C_6H_3O]_2$ | 2 | 465.77 | Deep yellow | 13.64 | 14.17 | 9.0 | 222 | 257 | 360 |
| Cu $[(NO_2)_3C_6H_2O]_2$ | 2 | 555.77 | Deep yellow | 11.43 | 11.18 | 5.5 | 204 | 238 | 356 |
| Zn $[(NO_2)C_6H_4O]_2$ | 1 | 359.60 | Deep red | 18,18 | 17.64 | 10.3 | 210 | 279 | 351 |
| Zn $[(NO_2)_2C_6H_3O]_2$ | 2 | 467.61 | Lemon yellow | 14.01 | 14.30 | 9.7 | 223 | 257 | 360 |
| Zn $[(NO_2)_3C_6H_2O]_2$ | 5 | 611.65 | Deep yellow | 10.69 | 9.89 | 4.9 | 204 | 238 | 356 |
| 2-nitrophenol | - | 139.11 | Lemon yellow | -- | -- | 1.9 | 209 | 279 | 351 |
| 2,4-dinitrophenol | - | 184.11 | Golden yellow | -- | -- | 2.3 | 207 | 257 | 360 |
| 2,4,6-trinitrophenol | - | 229.10 | Deep yellow | -- | -- | 9.7 | 206 | 238 | 356 |

Estimation of Water of Crystallisation in Nitrophenates of Transition Metals.

The percentage of moisture in the transition metal nitrophenates (preserved under vaccum) was found out by using Karl-Fisher titrator (METTLER DL-18) by taking methanol (Qualigens) as solvent. Each titration was repeated till concordent value was obtained. The water of crystallisation was calculated from the following relation and the data are given in the Table.

$$\text{water of crystallisation} = \frac{\%\text{ of moisture} \times \text{Mol. wt. of the sample}}{100 \times 18.015}$$

UV Spectral Studies of Nitrophenates of Transition Metals and Nitrophenols.

The UV spectra of metal nitrophenates and nitrophenols were taken on HITACHI U-2000 spectrophotometer by using doubly distilled water and the $\lambda_{max}$ values are summarised in the Table.

## RESULTS AND DISCUSSION

The estimated values of percentage of each metal is quite comparable with the theoretical values (Table), which confirms the formation of metal nitrophenates. The question arises, whether these compounds are ionic or covalent or both. In order to decide this,

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conductivity measurments were carried out. Picric acid gave the higher value of conductivity as compared to 2,4-dinitrophenol and 2-nitrophenol. This trend has been found to be reversed by the introduction of metal ion in the nitrophenols. The low conductance value of TNP might be due to the bulky ring substituted phenoxy anion. However, these values clearly indicate the ionic nature of these compounds. The higher value of conductance of picric acid may be due to its lower acid dissociation constant ($pK_a$=0.419) as compared to 2,4-dinitrophenol ($pK_a$=4.08) and 2-nitrophenol ($pK_a$=7.222).

The water of crystallisation for each sample was found out quantitatively in order to study their role in thermal stability of transition metal nitrophenates. In every set of metal nitrophenates it was found that the TNP is more hydrated and MNP is least hydrated (Table). Moreover, some of the MNPs are non-hydrated. However, our results are not comparable with Silberrad[2] and Agrawal et.al.[4,5]

The $\lambda_{max}$ values obtained for these nitrophenate salts have good agreement with the $\lambda_{max}$ values of their corresponding nitrophenols, which shows that electronic structure of nitrophenols are not at all disturbed in the process of interaction. Everywhere three absorbtions are obtained in the region of 200(I), 260(II) and

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350 nm(III) bands. The I and II bands are associated with $\pi$ eletrons of the benzene ring and the III band may be due to the $n \rightarrow \pi^*$ transitions in nitro group(s). These values are exactly matching with the literature values.[12] Normally unsubstituted benzene[13,14] exhibits two intense absorbtion bands at about 180 and 200 nm and a weak absorbtion band arround 260 nm. All these bands are associated with electron system of benzene and are affected markedly by substitution. Substitution is supposed to pertrub the benzene ring both by resonance and inductive effects and consequently 200 and 260 nm bands are shifted. Resonance effects apparantly cause greater changes in the spectra than inductive effects.[15,16] The 260 nm band is mainly affected by the resonance effect of substitutions, with polar groups containing unshared electrons (auxochromes like -OH), shifts the band to longer wavelength and also intensifies them. In every set of metal nitrophenates, the intensity of 260 nm(II) band is in the order TNP>DNP>MNP, which indicates the increase in the resonance effect with the number of nitro groups. While comparing the spectra of 2,4-dinitrophenol and DNPs, the I band observed in DNPs is broadened and also shifted from 207 to around 220 nm whereas, II and III bands are not disturbed. It may be due to the imbalanced resonance/inductive effect of the nitro groups at 2 and 4 positions of the phenoxy ion.

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Summarising the results, it can be concluded that nitrophenates of transition metals are ionic salts having variable water of crystallisation. The stoichiometry of these compounds has also been confirmed by thermogravimetric (TG) analysis.

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