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NITROPHENATES OF TRANSITION METALS
PART I. SYNTHESIS AND CHARACTERISATION

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ABSTRACT

A large number of nitrophenates of transition metals have been synthesised and characterised during the programme of formulation of new energetic materials. These compounds have been found to be ionic salts and number of water of crystallisation was found to depend upon the number of nitro groups.

INTRODUCTION

Interest in the systematic synthesis and characterisation of nitrophenates of transition metals (C-NO_2 explosives) 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,

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these are expected to be good candidates for propellant formulations. Although, nitrophenates of many metals are known but their structures are still controversial.

Agrawal and Agrawal[4] and Srivastava et al[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, having variable number of water 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.

In our programme of preparing new energetic materials[1,7-10] it was decided to synthesis nitrophenates of 3d-transition metals. Gravimetric estimation, Karl-Fischer titration, conductivity and UV spectral studies were undertaken in order to characterise these compounds. It has been found that all these compounds are purely ionic in nature and the presence of water molecules depends upon the number of nitro groups. These findings are contradictory to Silberrad[2] and other workers.[4,5]

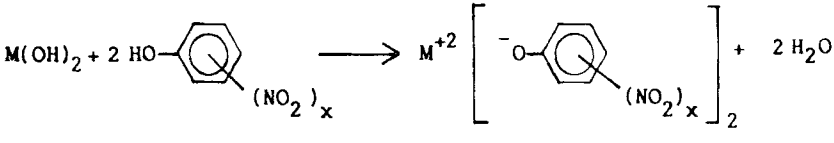
EXPERIMENTAL

Materials

Picric acid (BDH) and 2,4-dinitrophenol (Thomas Baker) were used as received without any further purification. 2-nitrophenol (BDH) was recrystallised from hot water, whenever required. Carbonates of nickel (Thomas Baker), zinc (Sarabhai), iron (Loba), cobalt, copper (BDH) and manganese acetate (Sarabhai) were used as such.

Synthesis of Nitrophenates of Transition Metals (NPTM).

Generally, nitrophenates are prepared by interacting transition metal cation with mono-, di- or tri-nitrophenol.[1-5] We have synthesised the nitrophenates of manganese, iron, 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.



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

Scheme

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 solutions with rotary vaccum evoporator (JSGW, Ambala) at low temperature (60 °C) and pressure (200 mm Hg). All the compounds were recrystallised in hot water. CAUTION! These compounds are highly explosive and should be handled with care.

Characterisation of NPTM.

The purity of NPTM was checked by thin layer chromatography (TLC), by using ethyl acetate (Qualigens) as eluent and coloured spots were obtained on TLC plates without any developing reagent. These compounds are of 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 molecules do not play any role towards their colours. The melting points could not be determined, as they start decomposing prior to melting. The precentage of each metal was estimated gravimetrically.[11] The formation of corresponding metal oxides was also confirmed by heating the samples of NPTM with Al_2O_3 (1:4 ratio) at a slow heating rate upto 600°C. Al_2O_3 was added as a diluent to avoid explosion.

The conductivity of these NPTM salts and corresponding nitrophenol 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.

The percentage of moisture in NPTM (preserved under vaccum) was found out by using Karl-Fischer 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.

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

The UV spectra of NPTM and corresponding nitrophenols were taken on HITACHI U-2000 byusing doubly distilled water and the λ_{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, conductivity measurments were carried out on NPTM and corresponding nitrophenols. 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 prove 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 NPTM. In every set of metal nitrophenates, it was found that the TNP is more hydrated and MNP is least hydrated. This seems to be due to H-bonding between NO_2 group(s) and water molecules. Moreover, some of the MNP are non-hydrated. However, our results are not matching with Silberrad[2] and others.[4,5]

The λ_{max} values obtained for these NPTM salts are in good agreement with the λ_{max} values of their corresponding nitrophenols, which shows that electronic structure of nitrophenols are not at all disturbed by incorporation of the metal in the latter. Everywhere, three absorbtions are obtained in the region of 200(I), 260(II) and 350 nm(III) bands. The I and II bands are associated with π electrons of the benzene ring and the III band may be due to the $n \rightarrow \pi^*$ transitions due to 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 around 260 nm. All these bands are associated with π electron system of benzene and are affected markedly by substitution, which may be due to the perturbation of the benzene ring both by resonance and induction, 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), which 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 increase of the resonance effect with the number of nitro groups. While comparing the spectra of 2,4-dinitrophenol and DNP, the I band observed in DNP is broadened and also shifted from 207 to around 220 nm whereas, II and III bands are not distrubed. It may be due to the imbalanced resonance/inductive effect of the nitro groups at 2 and 4 positions of the phenoxy ion.

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

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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 Crystallisation	Mol. Wt.	Colour	% of Metal		Conductance $\mu \Omega^{-1} cm^{-1}$	λ_{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

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