

2,4- and 3,5-Dinitrobenzoates of Cd, Mn, Ni and Co

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2,4- and 3,5-dinitrobenzoates of Co, Ni, Mn and Cd were obtained as hydrated salts with a metal : ligand ratio of 1 : 2. They were found to be trihydrates of a yellow colour for 2,4-dinitrobenzoates and tetrahydrates with colours characteristic of M^{2+} ions for 3,5-dinitrobenzoates. The carboxylate group appears to be a bidentate chelating ligand. The NO_2 groups do not coordinate with metal ions. Dinitrobenzoates of Co, Ni, Mn and Cd are crystalline compounds characterized by low symmetry and a large size of unit cells. They are unstable compounds that melt above 573 K and decompose explosively. In two steps, they lose the crystallization water molecules. Decomposition of the dinitro complexes yields, as final products, the oxides of appropriate metals. The solubilities in water at 293 K for all complexes are in the order of: $10^{-1} - 10^{-2} \text{ mol dm}^{-3}$.

INTRODUCTION

2,4-Dinitrobenzoic acid is a yellow crystalline solid readily soluble in hot water but sparingly soluble in cold water. Its electrolytic dissociation constants are equal to $3.85 \cdot 10^{-2}$ ($t = 25^\circ\text{C}$) and $3.2 \cdot 10^{-2}$ ($t = 40^\circ\text{C}$), respectively.¹⁻⁴ The compounds of 2,4-dinitrobenzoic acid are comparatively little known. From a survey of the literature it follows that there are papers on its salts with the following cations:^{1,5-9} Na^+ , Mg^{2+} , Ba^{2+} , NH_4^+ , K^+ , Pb^{2+} , Y^{3+} , La^{3+} , Ce^{3+} – Lu^{3+} and Sc^{3+} .

3,5-Dinitrobenzoic acid is a white crystalline solid sparingly soluble in water¹ and its electrolytic dissociation constant is equal to $1.63 \cdot 10^{-3}$ ($t = 25^\circ\text{C}$). The literature informs about its salts with the cations:^{1,10-28} Na^+ , NH_4^+ , K^+ , Ag^+ , Cu^{2+} , Pb^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Mn^{2+} , Ni^{2+} , Hg^{2+} , Y^{3+} , La^{3+} , Ce^{3+} – Lu^{3+} and Sc^{3+} . Only the 3,5-dinitrobenzoates of Mn¹ and Ni¹⁴ appear to have been isolated in the solid state.

2,4-Dinitrobenzoic acid is stronger than 3,5-dinitrobenzoic acid as a result of the steric effect of NO_2 group in ortho-position in the benzene ring.⁴ The aim of this work was to obtain the complexes of Mn, Co, Ni and Cd with 2,4- and 3,5-dinitrobenzoic acids in solid state with a metal : ligand ratio of 1 : 2, and to examine some of their physico-chemical properties.

EXPERIMENTAL

The 2,4- and 3,5-dinitrobenzoates of Ni, Co, Mn and Cd were prepared by addition of equivalent amounts of 0.2 ammonium dinitrobenzoate ($\text{pH} \approx 5$) to a hot solution containing divalent ions of Co, Ni, Mn and Cd nitrates and by crystallization at 293 K. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant mass. The contents of carbon, hydrogen and nitrogen were determined by elemental analysis with V_2O_5 as oxidizing agent. Element contents were established by gravimetry (using ammonium phosphate for Mn^{2+} determination, sodium anthranilate to determine Co^{2+} and dimethylglyoxime for Ni^{2+} determination) or polarography (for Cd^{2+} determination). All dinitrobenzoates of Cd, Ni, Co and Mn are hydrated salts with a metal to ligand ratio of 1 : 2 (Table I).

TABLE I
Analytical data

Complex	% H		% C		% N		% M		% H ₂ O	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Mn L ₂ · 3H ₂ O	2.52	2.48	35.29	35.30	10.88	10.92	11.55	11.60	11.34	11.42
Mn L ₂ * · 4H ₂ O	2.55	2.45	30.60	30.40	10.20	10.30	10.01	10.00	13.11	13.01
Cd L ₂ · 3H ₂ O	2.03	1.98	28.55	28.48	9.51	9.60	19.10	19.01	9.17	9.05
Cd L ₂ * · 4H ₂ O	2.30	2.21	27.70	28.00	9.23	9.30	18.53	18.70	11.87	12.02
Ni L ₂ · 3H ₂ O	2.24	2.30	31.41	31.50	10.47	10.38	10.97	11.00	10.09	9.98
Ni L ₂ * · 4H ₂ O	2.53	2.70	30.39	30.60	10.13	10.28	10.62	10.48	13.02	13.00
Co L ₂ · 3H ₂ O	2.24	2.15	31.40	31.00	10.46	10.30	11.01	10.02	10.09	9.48
Co L ₂ * · 4H ₂ O	2.64	2.52	30.38	30.44	10.12	10.20	10.65	10.80	13.02	12.88

L: 2,4-C₇H₃N₂O₆

L*: 3,5-C₇H₃N₂O₆

2,4-Dinitrobenzoates of Cd, Mn, Co and Ni form trihydrates whereas 3,5-dinitrobenzoates form tetrahydrates. 2,4-Dinitrobenzoates have a yellow colour while 3,5-dinitrobenzoates colours characteristic of the corresponding divalent ions. In order to confirm the chemical composition of the salts, the IR spectra of the hydrated and anhydrous complexes, dinitrobenzoic acids and their sodium salts, and also of sodium nitrite, were recorded in the 4000–400 cm^{-1} range using KBr discs on an UR-20 spectrophotometer (Tables II, III). In order to study the crystal structure of hydrated and anhydrous dinitrobenzoates of Cd, Mn, Co and Ni, and the structures of

TABLE II
Frequencies of the absorption bands of CO and NO₂ groups
for 2,4- and 3,5-dinitrobenzoic acids (ν/cm^{-1})

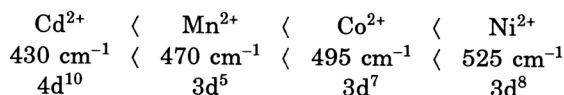
Dinitrobenzoic acids	$\nu_{\text{C=O}}$	$\nu_{\text{as NO}_2}$	$\nu_{\text{s NO}_2}$	$\Delta\nu_{\text{NO}_2}$
2,4-	1730	1540	1350	190
3,5-	1706	1550	1350	200

RESULTS AND DISCUSSION

The 2,4- and 3,5-dinitrobenzoates of Ni, Co, Cd and Mn were obtained in the crystalline form with the general formula: $M(C_7H_3N_2O_6)_2 \cdot nH_2O$, where $M = Ni, Co, Mn$ and Cd and $n = 3, 4$. Their formulae were established on the basis of the IR spectra data and the results of elemental analysis (Table I – III). All dinitrobenzoates were found to be crystalline and coloured hydrates. The 2,4-dinitrobenzoates of Mn, Cd, Co and Ni form yellow trihydrates whereas 3,5-dinitrobenzoates form tetrahydrates with colours typical of the corresponding M^{2+} ions. For all the salts investigated, the number of the crystallization water molecules increases in the order: 2,4-dinitro- < 3,5-dinitro-, smoothly with the change of the NO_2 group position in the benzene ring. Also, the colour of dinitrobenzoates depends on the position of NO_2 groups. When the NO_2 group is not accompanied by another substituent in the benzene ring and the molecule is planar, the NO_2 group electrons are conjugated with the Π electrons, thus causing a decrease in the electron density in the benzene ring and bathochromic shifts with respect to unsubstituted benzene compounds.^{4,29-31} The colour of the 2,4-dinitrobenzoates of Co, Ni, Cd and Mn is yellow and is mainly caused by the NO_2 group in ortho position. In these molecules, the arrangement of the substituents is not coplanar with the benzene ring because of the steric effects resulting from the NO_2 group in ortho position.⁴ The NO_2 group electrons are not conjugated with the Π electrons and, thus they can be easily excited by visible light.^{4,29,31-39} The presence of the second NO_2 group in the benzene ring does not cause changes in the complex colour because, irrespective of the number of the NO_2 groups in the benzene ring, only one group may influence the electron density in the compound. Therefore, 2,4-dinitrobenzoates and 2-nitrobenzoates of Ni, Co, Cd, Mn have a yellow colour.⁴⁰ However, the molecules of 3,5-dinitrobenzoates have a planar structure since steric effects disappear because the NO_2 groups are in 3- and 5-positions and the NO_2 group electrons are conjugated with the Π electrons. In these molecules, the $d \rightarrow d$ electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave-lengths, which depends on the nature of the metal ion. Thus, the colours of the complexes are those typical of the appropriate divalent ions.

The IR spectra of 2,4- and 3,5-dinitrobenzoates are not the same. Differences in the frequencies of the characteristic bands result from the changes in the dipole moment values of the dinitro acids related to the position of the NO_2 groups. Having a strong inductive effects, the NO_2 group attracts electrons, thus forming a dipole; its moment is the greatest when the NO_2 group is in para position. Bands of the CO group vibrations are displaced from 1706 cm^{-1} (3,5-dinitrobenzoic acid) to 1730 cm^{-1} (2,4-dinitrobenzoic one). The IR spectra of acids differ clearly from each other in the range of aromatic bands. The bands arising from asymmetric and symmetric vibrations of the NO_2 group occur at $1550\text{--}1540\text{ cm}^{-1}$ and 1350 cm^{-1} , respectively. When the acids form salts, their IR spectra are changed. The CO bands disappear, which indicates that no COOH group is present in the complexes. The bands of the asymmetric and symmetric COO^- group vibrations occur at $1615\text{--}1595\text{ cm}^{-1}$ and $1430\text{--}1420\text{ cm}^{-1}$, respectively. The bands at $1550\text{--}1530\text{ cm}^{-1}$ and $1360\text{--}1350\text{ cm}^{-1}$ arise from asymmetric and symmetric NO_2 group vibrations. The small values of displacements in the position of $\nu_{as}(NO_2)$ or their lack for $\nu_{as}(NO_2)$, compared to those in the dinitro acids, indicate that there is no coordination of the NO_2 groups with the metal ions. Small splittings of $\nu_{as}(NO_2)$ bands may presumably result from the inter-

action of the ligands and water molecules in the complexes and from their polar properties. Broad absorption bands with the maxima at 3700–3200 cm^{-1} confirm the presence of crystallization water. Bands of aromatic ring vibrations are observed at 1650–1620 cm^{-1} , 1555–1465 cm^{-1} and 1080–1060 cm^{-1} , respectively. The bands at 1170–1100 are indicative of $\beta(\text{C-H})$ vibrations while those at 750–725 cm^{-1} confirm the $\gamma(\text{C-H})$ ones. The aromatic ring vibration $\nu(\text{C-C})$ bands and the bands of $\beta(\text{C-H})$ and $\gamma(\text{C-H})$ vibrations in the IR spectra of 2,4- and 3,5- dinitrobenzoates of Co, Ni, Mn and Cd are strong and similar to those in the parent acid spectra. This is probably due to the formation of some delocalized covalency bonds in the complexes.⁴¹ The greatest similarity in the aromatic vibration bands, as compared to those in parent acids, is observed for the dinitrobenzoates of nickel. The bands at 525–430 cm^{-1} confirm the M-O vibrations in dinitrobenzoates. These bands are shifted in each of the presented series. The shifts are the greatest for the Ni complexes and the smallest for the Cd complexes which is consistent with the relative stability of the M-O bonds. The frequency of the M-O bands increases in the order:



thus following the Irving-Williams order for divalent ions.^{31,42} This probably results from the different number of d electrons of metal ions, their electronegativities and the ionic radius size. The smaller the ionic radius, the bigger is its ionic potential that may influence the ligand forming the stronger M-O bond, which leads to higher band frequencies. Accordingly, 2,4- and 3,5-dinitrobenzoic acids form the most stable complexes with Ni and the weakest with Cd. Comparison of the M-O bond stabilities in the complexes seems possible because they are compounds of the same type. In these complexes, the M-O vibrations are not pure on account of the conjugation of C-O and C-C group vibrations. In a series of dinitrobenzoates, frequencies of the M-O bands increase in the order: 2,4-dinitro- \langle 3,5-dinitro- being changed smoothly with the change of the NO_2 group positions in benzene ring. Being the smallest for the 2,4-dinitro- isomer and the greatest for the 3,5-dinitro- ones, the frequencies of the M-O bands suggest that 3,5-dinitrobenzoic acid forms more stable complexes while 2,4-dinitrobenzoic acid the weakest. This is probably related to the nephelauxetic effect,^{31,42} which seems to be the strongest for the 3,5-dinitrobenzoate ligand. The greatest d electron delocalization is observed for Ni^{2+} ions. In Table III, the maxima for the asymmetric and symmetric vibrations of the COO^- group for 2,4- and 3,5- dinitrobenzoates of Ni, Co, Cd and Mn are presented. The magnitudes of separation, $\Delta\nu$ between the frequencies $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ in the complexes are lower than in the sodium salts, which indicates a smaller degree of ionic bond in the complexes in comparison with those for sodium. Having an ionic potential greater than a sodium ion, divalent ions influence the ligand more strongly, causing its greater deformation. In the IR spectra of 2,4- and 3,5-dinitrobenzoates, the shifts of the $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ frequencies are lower and higher, respectively, relative to those for sodium 2,4- and 3,5-dinitrobenzoates. Accordingly, the carboxylate ion seems to be a bidentate, chelating ligand.^{42,43} The values of $\Delta\nu$ for Cd and Mn dinitrobenzoates are changed in the order: 3,5-dinitro- \rangle 2,4-dinitro- and they are greater for Mn^{2+} ions. The COO^- ion is a bidentate chelating ligand with probably incomplete equalization of its bond

lengths. The least values of $\Delta\nu$ for 2,4-dinitrobenzoate of Ni and 3,5-dinitrobenzoate of Co are indicative of the greatest symmetrization of the OCO group structure caused by the increase of the M-O bond covalency. It results from the greatest concentration of d electrons, which leads to a more complete equalization of OCO bond lengths. From the values of $\Delta\nu$ it is not possible to define the degree of the covalent bond because of the changes of the OCO bond angle with the changes of ionic radii of elements. To verify that the obtained 2,4- and 3,5-dinitrobenzoates do not undergo isomerization (during precipitation or on heating to 573 K),⁴⁴⁻⁴⁶ the IR spectra for hydrated and dehydrated complexes and for sodium nitrite were studied. As a monodentate ligand, the nitrite ion may bond either through nitrogen, forming a nitro complex, or through the oxygen atom, yielding a nitrito one.⁴⁴ The results reveal that dinitrobenzoates isolated as solids form nitro complexes and no transformation process of nitro to nitrito group takes place with rising temperature.

From the diffractogram analysis, both the hydrated and anhydrous dinitrobenzoates of Ni, Co, Cd and Mn were found to be crystalline compounds characterized by low symmetry, a large size of unit cells, different structures and various degrees of crystallinity.⁴⁷ The anhydrous dinitrobenzoates appear to be less crystalline than the hydrated ones. No changes of their structures, as compared to the hydrated salts, were observed. Accordingly, all dinitrobenzoates heated at 273–573 K do not form nitrito complexes and the loss of crystallization water molecules does not modify their crystalline structure.

Dinitrobenzoates of Ni, Co, Mn and Cd are stable up to 573 K, after which they are explosively decomposed at the melting point. Roasted in air at 1173 K, they form oxides of appropriate metals which are the final products of their decompositions: NiO, Co₃O₄, CdO and Mn₂O₃, whose structures were identified roentgenographically.⁴⁷ The thermal stability of dinitrobenzoates was studied in air at 273–573 K (Table IV). Figure 1 exhibits the derivatogram of nickel 2,4-dinitrobenzoate trihydrate.

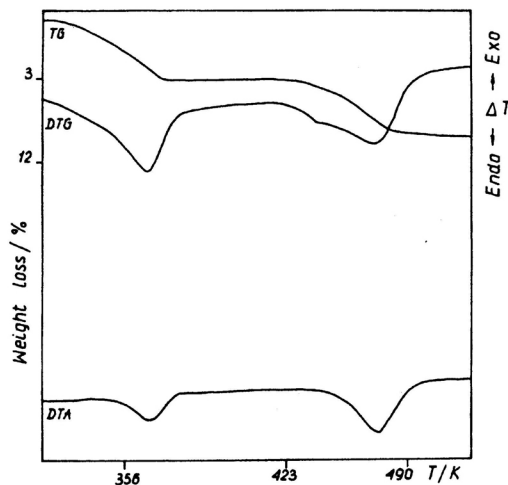


Figure 1. TG, DTG and DTA curves of nickel 2,4-dinitrobenzoate trihydrate.

hydrate. Dinitrobenzoates of Ni, Co, Cd and Mn are dehydrated in two steps. 2,4-Dinitrobenzoate trihydrates, losing first one molecule of water (317–422 K), form dihydrates that then expel the remaining two ones (390–495 K) to yield anhydrous complexes. In the first step of dehydration (310–380 K), 3,5-dinitrobenzoate tetrahydrates release two water molecules forming dihydrates which then, in the second stage of dehydration (380–455 K), lose the remaining two ones and form anhydrous salts. The dehydration process is related to the endothermic effect. In a series of 3,5-dinitrobenzoates, in the first step of dehydration, the least thermally stable is the complex of Mn that starts losing the two molecules of water at 310 K. The most thermally stable is the cobalt 3,5-dinitrobenzoate, which starts to dehydrate at 330 K. In the case of 2,4-dinitrobenzoates, in the first step of dehydration, the least thermally stable is the complex of Cd which releases one water molecule at 317 K whereas the most thermally stable is the complex of cobalt which expels water at 328 K. In the second stage of dehydration (390–495 K), the least thermally stable is cobalt 2,4-dinitrobenzoate while cadmium 2,4-dinitrobenzoate is the most thermally stable. For 3,5-dinitrobenzoates, in the second step of dehydration (380–455 K), the complex of Mn expelling water molecules at 380 K is the least thermally stable while the most thermally stable is the complex of cadmium which starts to dehydrate at 390 K. Being lost at comparatively low temperatures and in two stages, water molecules seem to be outer-sphere water and occupy various positions in the same coordination sphere of the complexes in which they are differently bound. The anhydrous 2,4-dinitrobenzoates of Ni, Co, Cd and Mn are formed in a temperature range from 465 K (for Co) to 505 K (for Cd) while anhydrous 3,5-dinitrobenzoates of these elements in a range from 458 K (for Mn) to 470 K (for Ni). The temperature of anhydrous complex formation does not regularly change with the ionic potential of elements (Figure 2). Its values, higher for 2,4-dinitrobenzoates than for 3,5-dinitrobenzoates, suggest that the water molecules are more strongly bound in the 2,4-dinitrobenzoates than in the 3,5-dinitrobenzoates. In the case of 3,5-dinitrobenzoates of Mn, Co and Ni, the temperature values of anhydrous salt formations obey the Irving-Williams sequence,^{31,42,48} $Mn^{2+} < Co^{2+} < Ni^{2+}$. The smaller the element radius, the stronger the water molecules are bounded by that ion.

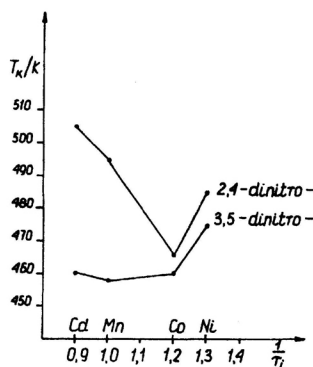


Figure 2. Interdependence of the temperature of anhydrous salt formation for 2,4- and 3,5-dinitrobenzoates of Mn, Co, Ni and Cd and the ionic potential of the element.

Solubilities of 2,4- and 3,5-dinitrobenzoates of Ni, Co, Cd and Mn are in the orders of: 10^{-1} mol dm^{-3} for 2,4-dinitrobenzoates and 10^{-2} mol dm^{-3} for 3,5-dinitrobenzoates (Table IV, Figure 3). Being greater for 2,4-dinitrobenzoates than for 3,5-dini-

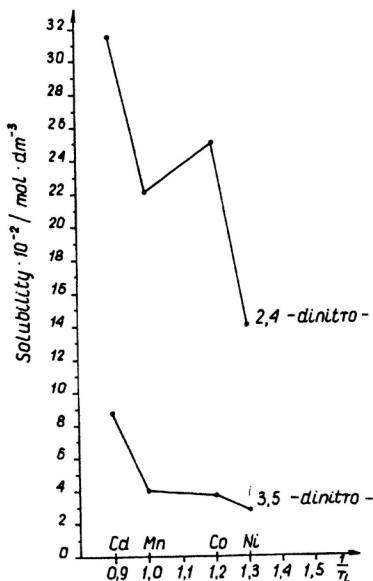


Figure 3. Relationship between the solubilities of 2,4- and 3,5-dinitrobenzoates of Mn, Ni, Co and Cd and the ionic potential of the element.

trobenzoates, the solubility values vary parallel to the changes of electrolytic dissociation constants of the parent acids: $K_{2,4\text{-dinitro-}} > K_{3,5\text{-dinitro-}}$. The 2,4-dinitrobenzoic acid is stronger than the 3,5-dinitrobenzoic acid. Different strengths of these acids result from the various NO_2 group positions in the benzene ring, which causes a different influence of the steric, mesomeric or inductive effects of substituents on electron density in the compounds. In the 2,4-dinitrobenzoic acid, the greater decrease of electron density than in the 3,5-dinitrobenzoic acid is due to the prevalent influence of steric effects caused by the NO_2 group in ortho- position. In the series of 2,4- and 3,5-dinitrobenzoates of Cd, Mn, Co and Ni, the complexes of Cd are the most soluble and the complexes of Ni the least soluble. The smallest values observed for Ni complexes are probably related to the reduced ionic character of the Ni-O bond.

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SAŽETAK

2,4- i 3,5-dinitrobenzoati kadmija, mangana, nikla i kobalta*Wiesława Ferenc*

2,4- i 3,5-dinitrobenzoati kadmija, mangana, nikla i kobalta dobiveni su kao hidratne soli u kojima je omjer metal : ligand = 1 : 2. Nađeno je da su 2,4-dinitrobenzoati trihidrati žute boje, dok je boja u 3,5-dinitrobenzoata – tetrahidrata boje karakteristične za ione M^{2+} . Karboksilna skupina bidentatni je kelatni ligand. Skupina NO_2 ne koordinira metalne ione. Dinitrobenzoati kobalta, nikla, mangana i kadmija kristalni su spojevi niske simetrije i velikih jediničnih ćelija. To su nestabilni spojevi koji se tale pri 573 K, a raspadaju se eksplozivno, gubeći kristaliničnu vodu u dva koraka. Raspad dinitro-kompleksa daje kao konačne produkte okside odgovarajućih kovina. Topljivost svih proučavanih kompleksa u vodi kod sobne temperature jest oko $(10^{-1} \dots 10^{-2})$ mol dm^3 .