Review

Nitroderivatives of Catechol: from Synthesis to Application

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Received: 03-03-2011

Abstract

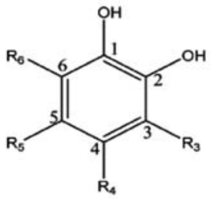
Nitroderivatives of catechol (NDCs) are reviewed with special emphasis on their complexes and applications. Binary, ternary and quaternary NDC complexes with more than 40 elements (aluminum, arsenic, boron, beryllium, calcium, cobalt, copper, iron, gallium, germanium, magnesium, manganese, molybdenum, niobium, rare earth elements, silicon, tin, strontium, technetium, thallium, titanium, uranium, vanadium, tungsten, zinc and zirconium) are discussed and the key characteristics of the developed analytical procedures – tabulated. The bibliography includes 206 references.

Keywords: Nitrocatechol, dinitrocatechol, complexes, spectrophotometric analysis, catabolic degradation, stability constants

1. Introduction

Nitroderivatives of catechol (NDCs) are important aromatic compounds, which contain two hydroxyl groups in ortho position and at least one nitro group directly attached to the benzene ring. NDCs belong to both the group of nitroaromatic compounds and the group of ortho diphenols. This interstitial position causes a certain inconvenience when searching for information in electronic and other databases because various names (systematic and non-systematic) have been used for these compounds {e.g. 4-nitrocatechol could be found as 4-nitrobenzene-1,2-diol (systematic name), 4-nitropyrocatechol, 1,2-dihydroxy-4-nitrobenzene or 2-hydroxy-5-nitrophenol}. On the other hand, the data existing on NDCs are scattered in many research fields – analytical chemistry, biochemistry, coordination chemistry, environmental chemistry, enzymology, organic chemistry, pharmacology, etc. A number of review articles and books have been published concerning different aspects of nitroaromatic[1–6] and phenolic compounds[7–10], however, there has not been a review on NDCs. Information on NDCs (synthesis, physical and spectral characteristics, complex forming ability, partici-

Table 1. Simple NDCs in the present review

General formula	Names and abreviations	R_3	R_4	R_5	R_6	Mol. mass	Melting point/ °C
	3-nitrobenzene-1,2-diol (3-nitrocatechol, 3-NC)	NO_2	H	H	H	155.11	86–87
	4-nitrobenzene-1,2-diol (4-nitrocatechol, 4-NC)	H	NO_2	H	H	155.11	174–176
	3,4-dinitrobenzene-1,2-diol (3,4-dinitrocatechol, 3,4-DNC)	NO_2	NO_2	H	H	200.11	147–148
	3,5-dinitrobenzene-1,2-diol (3,5-dinitrocatechol, 3,5-DNC)	NO_2	H	NO_2	H	200.11	166.8–167.1
	4,5-dinitrobenzene-1,2-diol (4,5-dinitrocatechol, 4,5-DNC)	H	NO_2	NO_2	H	200.11	166.5–167.5

pation in biochemical events, applications as analytical reagents and therapeutic tools, etc.) is systematically presented here. Simple NDCs (Table 1) are considered in more details; they have been in scope of author's interest for a long time.

2. Synthesis and Production

Numerous chemical[11–32] and bio-catalytic procedures[33–35] for synthesis of NDCs have been described. Catechol was first nitrated by Benedikt[11] using a nitration mixture of potassium nitrate and sulfuric acid. It was not recognized at first that two isomers, with different melting points, are formed: 3-NC and 4-NC. These isomers were separated by liquid-liquid extraction: 3-NC is readily soluble in petroleum ether, while 4-NC is soluble in water.[12,13] A method of preparation of 3,4-DNC with 24% yield (with respect to dihydrate: 3,4-DNC.2H_2O) was proposed by Rosenblatt at al.[13] Several reliable methods for synthesis of the other dinitroderivative, 3,5-DNC, were reported in 1972.[14–16] A higher yield (ca. 70%) was achieved by Nazarenko et al.[16] Many researchers have been using this method in spite of the fact that 3,5-DNC is commercially available. 3-NC, 4,5-DNC, 4-methyl-5-NC, 4-NC and some 4-NC derivatives (4-NC sulfate, 4-NC sulfate dipotassium salt) are also commercial products. Chemical industries in several countries produce these reagents, and their price, in most cases, makes them accessible for any laboratory.

3. Participation in Catabolic Events

Simple NDCs such as 4-NC,[35-49] 3-NC,[34,48] 4-methyl-5-nitrocatechol,[50–58] 3-methyl-4-nitrocatechol[58] and 4-nitropyrogallol[59] have been detected in environmental, industrial or model systems as intermediates in biological[41–59] and non-biological[36–40] degradation of various nitrogen-containing compounds (nitrobenzene, 4-nitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,6-dinitrophenol, azobenzene, etc.). In some cases, accumulation of NDCs (3-NC[34], 4-NC[35], 4-nitropyrogallol[59]) was observed. Some bacterial strains were isolated that could utilize 4-NC as a sole carbon, nitrogen and energy source: *Rhodococcus wratislaviensis* J3[60], *Rhodococcus opacus* J2[61], *Pseudomonas cepacia* RKJ200[44] and *Ochrobactrum* sp. B2.[62]

4. Physical and Spectral Characteristics

NDCs are yellow crystalline compounds that are stable under ordinary conditions (3,4-DNC is reported somewhat hygroscopic[13]). They are readily soluble in various organic solvents. Some of them are soluble in water (e.g. 4-NC, 3,4-DNC). The melting point and thermal stability of NDCs depends on the position of nitro group(s) in the catechol skeleton and the number of substituents. 3-NC, in which OH groups and NO_2 are located at neighbor carbon atoms, has the lowest melting point (Table 1). Information about the thermal behavior[63] and standard molar enthalpies of combustion and sublimation[64] of 4-NC has been presented in the literature.

Acidic dissociation of aqueous NDCs has been investigated repeatedly.[13,15,65–82] They are weak diprotic acids (Table 2). However, in comparison to catechol, these compounds are more acidic and less susceptible to oxidation.[84] Hydrogen bonding between OH groups or between an OH group and a nitro group ortho to it has been discussed in the literature.[12,75,80,84,85] Detailed information about the changes in the molecular structure of 4-NC, which take place during its deprotonation in aqueous solutions, was obtained by Cornard et al.[84] The authors showed that the 4-NC ring has a pronounced aromatic character, while the ring of 4-nitrocatecholate monoanion has a quinoidal character. The C_2-C_3 and C_5-C_6 (see general formula in Table 1) bond lengths in the monoanion are significantly shorter than those of the other bonds in the benzene ring. C-N and C_1-O bond lengths also become shorter. The two N-O bonds remain quasi identical but their lengths considerably increase upon first deprotonation. The second deprotonation intensifies the electronic redistribution and the benzene ring adopts a more marked quinoidal structure.

The spectral properties of 4-NC at different conditions correspond to the changes in the molecular structure mentioned above. Benedikt[11], who first mentioned 4-NC, noted that this compound is yellow under acid conditions and red under alkaline conditions. Cooper and Tulane[76] investigated in details the action of 4-NC as a titration indicator. They concluded that 4-NC could be useful for titrations of strong acids with strong bases and strong acids with weak bases, but cannot be used in titrations of weak acids or solutions containing much carbon dioxide. Absorption UV/Vis spectra of 4-NC at different conditions have been given in several papers.[72,74,84–88] The spectrum in aqueous acidic solution consists of an intense broad band with two main components at 345 and 309 nm and another located at 238 nm. At higher pH a new band, which is characteristic of the mono-deprotonated form (λ_{max} = 426 nm), appears. The presence of isobestic points, at 280 and 372 nm, gives evidence of the equilibrium between the protonated and mono-deprotonated form. For pH values higher than 9, an oxidation of the catecholate function may lead to a decomposition of the molecule that prevents the observation of the doubly deprotonated form in the spectrum.[84] The spectrum of this form could be recorded under inert atmosphere.[87] An absorption band with λ_{max} at about 512 nm and isobestic point at 468 nm is characteristic for it.[72,87]

Table 2. Literature acid dissociation constants

Compound	pK_{H_2L}	pK_{HL}	Ionic strength/mol/l	Temp. /°C	Ref.
3-NC	6.65[a], 6.59[b]	11.20[a],11.17[b]	0.1 (KCl)	25	15
	6.47[b]	11.40[b]	0.1 (KCl)	25	65
	6.66[b]			25	13
4-NC	6.78[a], 6.86[b]	10.64[a], 10.71[b]	0.1 (KCl)	25	15
	6.7[b]	10.83[b]	0.1 (KCl)	25	66
	6.60[a]	10.74[a]	0.1 (KCl)	25	72
	6.70[a]	10.31[a]	1.0 (KCl)	25	72
	6.68[b]	10.70[b]	0.1 (KCl)	25	73
	6.62[b]	10.75[b], 10.79[a]	0.1 ($NaClO_4$)	25	74
	6.59[b]	10.75[b]	0.1 (KNO_3)	30	75
	6.56[a]	11.33[a]	–	25	76
	6.88[b], 6.74[a]	–	–	25	13
	6.84[b]	11.1[b]	0.1 (KNO_3)	20	82
3,4-DNC	5.39[b]	8.27[b]		25	13
3,5-DNC	3.60[a]	9.83[a]	0.1 (KCl)	25	15
	3.54[b]	9.85[b]	0.1 (KCl)	25	15
	3.39[b]	9.69[b]	0.1 (KCl)	25	73
	3.37[b]	9.64[b]	0.1 (KCl)	25	81
Catechol	9.28[b]	13.02[b]	0.2 (KCl)	25	73, 83

a – obtained spectrophotometrically; b – obtained potentiometrically

Solvatochromism of 4-NC in a set of 27 common solvents, including water, was investigated by Riedel and Spange.[89] The results showed that the longest-wavelenght UV/Vis absorption maximum is independent of the 4-NC concentration in the range 10^{-4} – 10^{-5} mol/L, what is an indication of lack of dye aggregation.

Raman spectra of 4-NC and its singly deprotonated form have been recorded.[84,86,87] A calculation of the vibrational frequencies allowed a complete assignment of the Raman spectra of these two forms of 4-NC.[84]

Surprisingly, the structural and spectral information for the other NDCs found in the literature is scarce. Absorption spectra of 3,5-DNC in acidic[21,90], neutral[21] and alkaline[21] solutions have been represented. The positions of the absorption maxima of 3-NC (300 and 400 nm), 3,4-DNC (350 nm) and 3,5-DNC (330 nm) at pH 5, 3 and 2 respectively have been reported.[16]

5. Complexes of NDCs and Their Analytical Application

Compounds containing a catechol moiety are well-known complex forming reagents.[9,10] If attached to the catechol skeleton, a nitro group delocalizes π-electrons to satisfy its own charge deficiency. As a result, the colour, acid and complexing properties of the compound change dramatically. This may be of significance for the development of more powerful analytical procedures. In fact, two NDCs, 4-NC and 3,5-DNC, have been included in the IUPAC list of the most important organic analytical reagents.[91]

It should be mentioned that NDCs chelate with many metal ions, showing relatively large stability constants for their lower basicity with respect to catechol and other catechol derivatives. This is presumably due to the resonance contribution of the nitro group to the stabilization of the chelate ring.[75] However, the analytical applicability of NDCs usually do not correlate with the complex stability. For example, 3-NC forms more stable complexes than 4-NC and 3,5-DNC, but its analytical application is limited only to preparation of uranium adsorbents from seawater.[92,93] Nazarenko et al.[16] compared the molar absorptivities (ε_{max}) of the Ge(IV) complexes with several NDCs. They found that $\varepsilon_{3\text{-NC}}$ (3600 L mol^{-1} cm^{-1}) is significantly lower than these of $\varepsilon_{3,5\text{-DNC}}$ (11600 L mol^{-1} cm^{-1}), $\varepsilon_{4\text{-NC}}$ (19200 L mol^{-1} cm^{-1}) and $\varepsilon_{3,4\text{-DNC}}$ (20200 L mol^{-1} cm^{-1}). This fact well explains the little application of 3-NC as reagent in spectrophotometric analysis. At the same time, the limited application of 3,4-DNC in the mentioned field is somewhat surprising. It could be attributed to difficulties which arise during its synthesis and purification and insufficient investigations on its ternary complexes.

The complexes of NDCs with more than 40 elements are described in Sections 5.1 – 5.29. The complex forming elements are listed in alphabetical order according to their chemical symbols; however, the Rare earth elements (RE) are given simultaneously (section 5.18). The application of some complexes in inorganic analysis is presented in Table 3.

When discussing the analytical application of NDCs, it should be mentioned that many enzymological studies[94–101] are based on the Robinson, Smith and Williams method[102], which utilizes potassium 2-hydroxy-5-nitrophenyl sulphate (nitrocatechol sulphate) as substrate, and follows the enzyme activity by the colorimetric estimation of the liberated red 4-NC anion ($\varepsilon_{510} = 1.26 \times 10^4$ L mol^{-1} cm^{-1}).[101,102]

Another analytical application of a NDC (4,5-DNC), which is not based on complex formation, is the synthesis of the Hg(II)-selective ionophore with improved pH behavior.[103]

5. 1. Complexes of Al

Complex formation in aqueous solutions between Al(III) and some NDCs (H_2L: 3-NC, 4-NC, 3,5-DNC) has been investigated by several authors.[72,73,104–106] 4-NC and 3-NC were found to form AlL^+, AlL_2^- and AlL_3^{3-} species,[104,105] while 3,5-DNC – only AlL_2^- and AlL_3^{3-} species.[73] The formation constants of the mentioned complexes (calculated at 25 °C and ionic strength 0.1 mol/L) are shown in Table 4. According to Downard et al.[106] another complex is formed between Al(III) and 4-NC at pH 6-11: $AlL_2(OH)^{2-}$. This complex remains a minor species when a greater than 3-fold excess of 4-NC over Al(III) is maintained. In fact, the formation of AlL_3^{3-} is almost quantitative at a pH close to 9 what allows Al(III) to be determined amperometrically in environmental samples[106] (Table 3).

The complexation between Al(III) and 4-NC at pH = 5 was studied by Cornard et al.[86] They used molecular spectroscopy combined with quantum chemical calculations. The formation of $AlL(H_2O)_4^+$ and $AlL_2(H_2O)_2^-$ was highlighted and a complete assignment of UV/Vis adsorption and Raman spectra of these complexes was proposed.

The adsorption of 4-NC onto Al(III)-bearing surfaces was investigated by Vasudevan and Stone.[107] The stoichiometry of surface complex formation and the intrinsic equilibrium constants for adsorption onto Al_2O_3 were determined: (>SL$^-$: log K^s_{intr} = 14.47; >SL^{2-}: log K^s_{intr} = 6.58).[107]

Table 4. Complex formation constants for the major complex species in the aqueous Al(III) – NDC (H_2L) system at 25 °C and 0.1 mol/L ionic strength obtained potentiometrically

Complexes	3-NC	4-NC	3,5-DNC
$[AlL]^+$	$\log\beta_1 = 14.7^{104}$	13.74[105] 13.75[106] 13.89[73] 13.3[72]	–
$[AlL_2]^-$	$\log\beta_2 = 26.3^{104}$	25.39[105] 25.44[106] 26.33[73] 24.82[72]	21.80[73]
$[AlL_3]^{3-}$	$\log\beta_3 = 35.81^{104}$	34.31[105] 34.38[106] 37.08[73] 33.70[72]	31.68[73]

Table 3. Analytical methods based on NDC complexes

Analyte	Reagent(s)	Method	pH	Working range / µg mL^{-1}	λ/ nm	$\varepsilon \times 10^{-4}$/ L mol^{-1} cm^{-1}	Remarks	Ref.
Al(III)	4-NC	Amperometric-FIA	9	0.01–0.22			Application: soil solutions and soil-derived fluvic acid	106
As(V)	4-NC+BG	LLE-spectrophotometric	8		637	10.9	Org. solvent: toluene; Sb, Bi, Cr and Pb interfere	108
B(III)	4-NC	Spectrophotometric	8.0–8.5	2–27	440		Non-linear calibration graph; Fe(III) and Al interfere	15
Gd(III)	3,5-DNC+RB	LLE-spectrophotometric	6.3–7.0		563	3	Org. solvent: Benzene+izobutanol (9:1); Small RB excess with respect to Gd(III); Application: Cd_2O_3/La_2O_3 mixture	160
Ge(IV)	4-NC+BG	LLE-spectrophotometric	6–7	0.07–0.35	630	13	Org. solvent: CCl_4	135
Ge(IV)	4-NC+MTT	LLE-spectrophotometric	2.5–3.9	0.15–1.88	410	5.11	Org. solvent: $CHCl_3$; Cr^{3+}, Cr(VI), Fe^{3+}, Mo(VI), V(IV,V), W(VI) I^- and Cl^- interfere	136
Ge(IV)	4-NC+TTC	LLE-spectrophotometric	4.0–4.5	0.2–3.0	420	2.88	Org. solvent: $CHCl_3$; Al^{3+}, Cr^{3+}, Cr(VI), Fe^{3+}, Mg^{2+}, Mo(VI), Sn(II,IV), V(V) and W(VI) interfere	137
Ge(IV)	3,5-DNC+BG	LLE-spectrophotometric	0.3[16] or 0.1[139] mol/L HCl	0.01–0.14[16] 0.004–0.02[139]	625	14.1	Org. solvent: CCl_4; Application: Industrial samples (slags[16], concentrates[16], high purity arsenic[139])	16, 139
Mo(VI)	4-NC+TV	LLE-spectrophotometric	1.2–2.6	0.31–3.1	440	2.06	Org. solvent: $C_2H_4Cl_2$; Application: steels	144
Mo(VI)	4-NC+BT	LLE-spectrophotometric	1.8–4.0	0.2–6.7	445	2.38	Org. solvent: $C_2H_4Cl_2$; Application: steels, ferromolybdenum	147
Mo(VI)	4-NC+TT	LLE-spectrophotometric	1.8–2.5	0.5–10.0	445	2.28	Org. solvent: $CHCl_3$; Application: model mixture	143
Mo(VI)	4-NC+MTT	LLE-spectrophotometric	2.1–3.4	0.2–7.0	440	2.41	Org. solvent: $CHCl_3$; Application: steels, ferromolybdenum	146
Mo(VI)	4-NC+INT	LLE-spectrophotometric	1.5–3.0	0.24–6.9	430	1.94	Org. solvent: $C_2H_4Cl_2$; Application: steels ferromolybdenum	145
Mo(VI)	3,5-DNC+RB	Flotation-spectrophotometric	1.8	Up to 0.3	555	21	Flotation with cyclohexane; Absorbance is measured in acetone; Application: biological materials	148
Nb(V)	4-NC+TV	LLE-spectrophotometric	0.25–1.25 mol/L H_2SO_4	0.41–4.54	440	1.59	Org. solvent: $C_2H_4Cl_2$; Masking with EDTA and ascorbic acid; Application: steels	154

Nb(V)	3,5-DNC+ oxalate+RB	Flotation-spectrophotometric	3.1	Up to 0.3	555	21. 0	Flotation with cyclohexane; Absorbance is measured in acetone; Application: geological materials	158
Sn(IV)	3,5-DNC+BG	LLE-spectrophotometric	0.1 (H_2SO_4)	0.02–0.7	630	17.5	Org. solvent: CCl_4; Masking with ascorbic acid; Application: silicate rocks	90, 163
Ti(IV)	4-NC+TV	LLE-spectrophotometric	1.4–1.8	0.20–2.00	440	4.4	Org. solvent: $CHCl_3$; Masking with ascorbic acid; Application: aluminium alloys	168
V(V)	4-NC+INT	LLE-spectrophotometric	5.0	0.2–2.6	400	1.7	Org. solvent: $CHCl_3$; Application: steels	172
V(V)	4-NC+MTT	LLE-spectrophotometric	4.4–4.8	0.12–1.2	400	3.13	Org. solvent: $CHCl_3$; Application: catalysts, steels	183
V(IV)	4-NC+NTC	LLE-spectrophotometric	4.75	0.5–3.0	605	1.15	Org. solvent: $CHCl_3$+BuOH (7:3); Application: steels	179
V(IV) and V (V)	4-NC+MTT	LLE-spectrophotometric	4.5–4.8	0.15–1.7	$390^{V(V)+V(IV)}$, $570^{V(IV)}$	$3.6^{V(V)390}$, $3.1^{V(IV)390}$, $1.7^{V(IV)570}$	Org. solvent: $CHCl_3$; LLE at deficiency of 4-NC towards MTT; Application: catalysts	182
V(V)	3,5-DNC+BG	LLE-spectrophotometric	1.3	Up to 0.3	630	17	Org. solvent: CCl_4; Application: alums	171
V(V)	3,5-DNC+RB	Flotation-spectrophotometric	2–2.5	Up to 0.3	555	21	Flotation with cyclohexane; Absorbance is measured in acetone; Application: vegetables	184
W(VI)	3,5-DNC	Spectrophotometric	1	0.2–3.2	400	1	Nb,Ta, Ti, Mo, V, Sn and Ge interfere	185
W(VI)	3,5-DNC+DAM	LLE-spectrophotometric	1	0.1–16	400	2	Org. solvent: $CHCl_3$; Ge, Sn, Ti, V, Nb and Mo interfere	186
W(VI)	3,5-DNC+TT	LLE-spectrophotometric	0.25–0.40 mol/l H_2SO_4	0.5–7.4	400	2.12	Org. solvent: $CHCl_3$; Application: steels	187
W(VI)	4-NC+TV	LLE-spectrophotometric	5.4	0.7–10.3	425–430	2.69	Org. solvent: $CHCl_3$; Application: steels, ferrotungsten	187
W(VI)	4-NC+MTT	LLE-spectrophotometric	1.2–3.6	0.9–8.8	415	2.8	Org. solvent: $CHCl_3$; Application: steels, ferrotungsten	188
Zr(IV)	3,5-DNC+ Ant	LLE-spectrophotometric	0.2 mol/l HCl	0.9–9.1	420	1.5	Org. solvent: $CHCl_3$; Masking with thioglycolic acid and NH_4F; Application: $VOSO_4$	189

Abreviations: 4-NC – 4-nitrocatechol; 3,5-DNC – 3,5-dinitrocatechol; Ant – antipyrine; BG – brilliant green; BT – 3,3'-[3,3'-dimetoxy(1,1'-biphenyl)-4,4'-diyl]-bis[2,5-diphenyl-2H-tetrazolium] chloride; DAM – diantipyrilmethane; FIA – flow injection analysis; INT – 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride; LLE – liquid-liquid extraction; MTT – 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide; RB – rhodamin B; TTC – 2,3,5-triphenyltetrazolium chloride; TV – 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium violet)

5. 2. Complexes of As

As(V) reacts with 4-NC in the ratio of 1:3 to form a univalent complex anion, which can be extracted with a cationic dye into organic solvents.[108] Nine catechol derivatives and four kinds of cationic dyes were examined. Among these reagents, 4-NC and brilliant green (BG) were found the most useful for determining trace amounts of As(V). The absorption maximum of the ternary complex in toluene is at 637 nm, and the molar absorptivity is 1.09 × 10^5 L mol^{-1} cm^{-1}.[108]

The interaction between As(III) and 4-NC was investigated potentiometrically by Votava et al.[109] The equilibrium constant for the equation $H_3AsO_3 + H_2L \leftrightarrow AsL(OH)_2^- + H^+ + H_2O$ (where H_2L = 4-NC) was determined to be pK = 9.49.

5. 3. Complexes of B

Boric acid was reported to form chelates with 3-NC[15], 4-NC,[15,89,110–113] and 3,5-DNC.[15] The equilibrium constants for the reaction $B(OH)_3 + H_2L \leftrightarrow BL(OH)_2^- + H^+ + H_2O$ (where H_2L = 3-NC, 4-NC, and 3,5-DNC) were determined by spectrophotometry at an ionic strength of 0.1 mol/land 25 °C: pK = 3.46 ± 0.1, 3.76 ± 0.1 and 1.65 ± 0.12, respectively.[15] Other authors reported slightly higher values for the reaction with 4-NC: 3.96 (20 °C, ionic strength 0.1 M)[112] and 3.91 (25 °C, ionic strength 0.1 M).[113] Pizer and Babcock[110] investigated the mechanism of the complexation between boric or phenylboric acid and a series of catechol derivatives, including 4-NC. They found that the complexes of $PhB(OH)_2$ have higher stability constants.

4-NC was used for spectrophotometric determination of boric acid.[15] The sensitivity and selectivity of the proposed procedure was reported similar to that obtained with other diphenolic reagents (pyrocatechol violet, pyrocatecholocarboxilic acid, tiron), however, the color is stable for a long time (4 hours at pH_{opt} = 8–8.5) and the optimum wavelength is in the visible range (440 nm).[15]

Riedel and Spange[89] prepared a 1:2-complex, $K[BL_2]$, by mixing solutions of 4-NC, $B(OH)_3$ and K_2CO_3. They studied the solvatochromism of the complex in 22 common solvents and noticed that hydrogen-bond donor solvents cause a hypsochromic shift of the UV/Vis bands, while increasing dipolarity/polarizability of the solvent induces a bathochromic shift.

5. 4. Complexes of Ba

Häkkinen[114,115] reported the formation of two Ba^{2+} complexes with 4-NC (H_2L), BaL and BaL_2^{2-}, and one Ba^{2+} complex with 3-NC – BaL. The corresponding stability constants determined potentiometrically at 25 °C and an ionic strength of 0.1 mol/l (KCl) are as follows: $\log\beta_1$ = 2.6 and $\log\beta_2$ = 4.9 (for the complexes with 4-NC)[114] and

$\log\beta_1 = 2.71$, (for the complex with 3-NC).[115] The aqueous system Ba^{2+}–3,5-DNC was investigated by the same author, however complex formation was not observed.[116]

5. 5. Complexes of Be

Complexation between Be(II) and NDCs (H_2L: 3-NC[115], 4-NC[105], 3,5-DNC[116]) in aqueous solutions at 25 °C and an ionic strength of 0.1 mol/l (KCl) was investigated potentiometrically by Häkkinen. Formation of four complexes with 3-NC, two complexes with 4-NC and two complexes with 3,5-NC was reported. The following stability constants were calculated for these complexes: i) $\log\beta_1 = 11.29$, $\log\beta_{1h} = 15.2$, $\log\beta_2 = 20.13$ and $\log\beta_{2h} = 25.0$ (for the complexes of 3-NC: BeL, $BeHL^+$, BeL_2^{2-} and $BeHL_2^-$, respectively); ii) $\log\beta_1 = 10.359$ and $\log\beta_2 = 18.273$ (for the complexes of 4-NC: BeL, and BeL_2^{2-}, respectively); and iii) $\log\beta_1 = 8.49$ and $\log\beta_2 = 15.28$ (for the complexes of 3,5-DNC: BeL, and BeL_2^{2-}, respectively). It should be mentioned that 3,5-DNC has been regarded as a potential chelation agent for beryllium in medical and environmental systems.[117] This reagent is considered capable of lowering beryllium tissue burden and environmental remediation of beryllium-contaminated environments, but may possess toxicity that would be of concern based on known data of similar nitrophenols.[117]

5. 6. Complexes of Ca

Ca^{2+} forms in aqueous medium two chelates with each of the reagents (H_2L) 3-NC[115], 4-NC[114] and 3,5-DNC[116]: CaL and CaL_2^{2-}. The values of their stability constants, determined at 25 °C and an ionic strength of 0.1 mol/l (KCl) are as follows: $\log\beta_1 = 4.42$ and $\log\beta_2 = 7.5$ (for the complexes of 3-NC); $\log\beta_1 = 3.79$ and $\log\beta_2 = 7.13$ (for the complexes of 4-NC); and $\log\beta_1 = 3.21$ and $\log\beta_2 = 5.88$ (for the complexes of 3,5-NC).

5. 7. Complexes of Cd

Häkkinen[104,105] investigated the complex formation in the aqueous systems Cd^{2+} – 3-NC and Cd^{2+} – 4-NC. He detected CdL and CdL_2^{2-} in both systems. Their stability constants were determined potentiometrically at 25 °C and an ionic strength of 0.1 mol/l (KCl): $\log\beta_1 = 6.73$ and $\log\beta_2 = 11.87$ (for the system containing 3-NC)[104], and $\log\beta_1 = 6.495$ and $\log\beta_2 = 11.279$ (for the system containing 4-NC).[105] Another complex, Cd(OH)L, with stability constant $\log\beta = 1.07$, was detected in the system containing 3-NC.[104]

5. 8. Complexes of Co

Co(II) was reported to form chelates with 3-NC[104], 4-NC[75,118], and 3,5-DNC[81], which could be expressed with the general formulae CoL, CoL_2^{2-} and CoL_3^{4-} (NDC = H_2L). The values of their formation constants are shown in Table 5.

Tyson and Martell[119] studied Co(II) – 4-NC catalyzed oxidation of 3,5-di-tert-butylcatechol (3,5-DTBP) to corresponding o-quinone (3,5-DTBQ): 3,5-DTBP + $0.5O_2 \rightarrow$ 3,5-DTBQ + H_2O. This reaction seems to be important, since it is one of the few non-enzymic reactions to give o-quinone without H_2O_2 accumulation. The absence of H_2O_2 in the above mentioned equation could be explained with the ability of Co(II) – 4-NC to catalyze its decomposition.[119]

Table 5. Complexes of Co(II) with NDC (H_2L: 3-NC, 4-NC, 3,5-DNC) in aqueous solutions and their formation constants obtained potentiometrically

Complexes		**3-NC**	**4-NC**	**3,5-DNC**
[CoL]	$\log\beta_1 =$	3.84[a][104]	7.48[a][118], 7.48[b][75]	6.43[a][81]
$[CoL_2]^{2-}$	$\log\beta_2 =$	13.58[a][104]	12.72[a][118], 12.79[b][75]	11.21[a][81]
$[CoL3]^{4-}$	$\log\beta_3 =$	16.6[a][104]	15.93[b][75]	14.49[a][81]

a – at 25 °C and 0.1 mol/l ionic strength (KCl)
b – at 30 °C and 0.10 mol/l ionic strength (KNO_3)

Table 6. Complexes of Cu(II) with NDC (H_2L: 3-NC, 4-NC, 3,5-DNC) in aqueous solutions and their formation constants obtained potentiometrically

Complexes		**3-NC**	**4-NC**	**3,5-DNC**
[CuL]	$\log\beta_1 =$	12.03[a][65]	11.70[a][66], 11.65[b][75]	10.04[a][81]
$[CuL_2]^{2-}$	$\log\beta_2 =$	22.33[a][65]	21.10[a][66], 20,93[b][75]	17.8[a][81]

a – at 25 °C and 0.1 mol/l ionic strength (KCl)
b – at 30 °C and 0.10 mol/l ionic strength (KNO_3)

5. 9. Complexes of Cu

Cu(II) forms in aqueous medium two chelates with each of the reagents 3-NC[65], 4-NC[66,75] and 3,5-DNC[81]: CuL and CuL_2^{2-}. The values of their formation constants are presented in Table 6. The intensive yellow coloration of the complex with 4-NC was used for determination of 4-NC in the presence of similar compounds, such as 4-nitroanisole and 4-nitrophenol.[120] Cu(II) forms also a strongly colored complex with 2-hydroxy-5-methyl-4-nitrophenol (NMC).[32] The complex formation was found independent of pH between 5.4 and 7.2. Since some enzymes (e.g. aryl-sulfate sulfohydrolase from the New Zealand mollusk) are not inhibited by low concentrations of cupric ion, the enzymatic hydrolysis of sulfate esters of NMC could be monitored continuously in the presence of cupric ions by following the formation of the yellow species.[32] A direct-colouring metal precipitation method for demonstration of arylsulphatases A and B based on the reducing capacity of 4-NC was proposed by Partanen.[121] In this method, 4-NC (liberated from 4-nitrocatechol sulphate) reduces ferricyanide to ferrocyanide, which in turn forms a brown precipitate with copper that indicates the enzyme activity.

Several ternary complexes, which contain Cu(II) and 4-NC, were studied as well. The additional reagents used are ethylenediaminediacetic acid[122], amino acids[123], N,N,N',N'-tetrabenzylethylenediamine and N,N,N',N'-tetramethylethylenenediamine.[124]

5. 10. Complexes of Fe

3-NC[115] and 4-NC[66,72,125] were reported to form two and three complexes with Fe(III), respectively. Their formulae and formation constants are presented in Table 7.

Table 7. Complexes of Fe(III) with NDC (H_2L: 3-NC, 4-NC) in aqueous solutions and their formation constants determined at 25 °C and 0.1 mol/l ionic strength

Complexes		3-NC	4-NC
$[FeL]^+$	$\log\beta_1 =$	15.71[a 115]	15.53[a 66], 16.95[b 72]
$[FeL_2]^-$	$\log\beta_2 =$	28.92[a 115]	28.63[a 66], 29.78[b 72]
$[FeL_3]^{3-}$	$\log\beta_3 =$	–	38.22[a 66], 39.19[b 72], 40.00[a 125]

a – obtained by potentiometry
b – obtained by spectrophotometry and potentiometry

The interaction between Fe(III)-bearing surfaces and 4-NC were observed by Vasudevan and Stone.[107] They determined the stoichiometry of surface complex formation and the intrinsic equilibrium constants for adsorption onto hematite ($>SL^-$: $\log K^s_{intr} = 13.87$) and goetite ($>SL^-$: $\log K^s_{intr} = 14.02$; $>SL^{2-}$: $\log K^s_{intr} = 7.12$).

High-spin tris(nitrocatecholato)ferrate(III) complexes were synthesized and studied by Kawabata et al.[126] with three 3-NC derivative antioxidants containing the following substituents in position 5: $-CH = CR_2$, $-CH_2CHR_2$, and $-CH_2CR'(R)''$. The authors showed that nitrocatechols with a conjugation structure could sequester the chelated iron more effectively than catechol and derivatives without the conjugation.

4-NC was examined as an active site probe for nonheme iron dioxygenases.[127] Several studies were concerned with complexes of Fe(III)-soybean lipoxygenases and 4-NC.[128–130] Fe(III)-soybean lipoxygenase-1 yields with 4-NC a green colored 1:1 complex, which shows at pH 7.0 absorption maxima at 385 nm and 650 nm.[128] The structure of soybean lipoxygenase-3 in complex with 4-NC was studied by Skrzypczak-Jankun et al.[130] X-ray analysis showed 4-NC near iron with partial occupancy, blocking access to Fe but not covalently bound to it.

5. 11. Complexes of Ga

Ga(III) is known to form complexes with 4-NC[131], 3,4-DNC[132], 3,5-DNC[132] and the nitrocatechol antioxidants mentioned in the previous subsection.[126] The equilibrium and kinetics for the reaction of excess Ga(III) with 4-NC (H_2L) to give monochelate in aqueous solution: $Ga^{3+} + H_2L \leftrightarrow GaL^+ + 2H^+$ was investigated over the pH range 2-3. The complex has an absorption maximum at $\lambda = 405$ nm ($\varepsilon = 9 \times 10^3$ L mol^{-1} cm^{-1}); however, the reaction was monitored at $\lambda = 420$ nm, where the contribution of free 4-NC is less than 5%.[131]

Ternary ion-association complexes between Ga(III), dinitrocatechol (3,4-DNC or 3,5-DNC) and brilliant green (BG) were studied by Nazarenko et al.[132] Molar absorptivity coefficients of the complexes extracted in toluene were calculated: $\varepsilon_{650} = 8 \times 10^4$ l mol^{-1} cm^{-1} (for the complex with 3,4-DNC) and $\varepsilon_{650} = 7 \times 10^4$ l mol^{-1} cm^{-1} (for the complex with 3,5-DNC). [132] The molar ratio between the components in both complexes was found to be Ga:DNC:BG = 1:3:3.

5. 12. Complexes of Ge

Complexation between Ge(IV) and NDCs has been studied by many authors. Binary and ternary complexes with participation of 3-NC[16,133], 4-NC[16,67,111,133–137], 3,4-DNC[16,138] and 3,5-DNC[16,139] were reported and several procedures for Ge(IV) determination were proposed[16,133,135–137,139] (Table 3). The most sensitive germanium determination was achieved with 3,5-DNC and brilliant green ($\varepsilon_{625} = 1.41 \times 10^5$ l mol^{-1} cm^{-1}). However, Ge should be preliminary separated from interfering ions by LLE-extraction into CCl_4 and reextraction into water.[16,139] The complex has a molar ratio between the components 1:3:2 (Ge:3,5-NC:BG). All other studied ternary complexes have similar composition and could be represented with the general formula $(OC^+)_2[Ge(NDC)_3]^{2-}$ (where OC^+ is organophilic cation, which derives from tetrazolium salt or basic dye). Some equilibrium constants (association constant – β, distribution constant – K_D, extraction constant – K_{ex}) were calculated for the LLE systems with participation of tetrazolium salts: $\log \beta = 9.6$, $\log K_D = 1.52$ and $\log K_{ex} = 11.12$ (for the Ge(IV) – 4-NC – 2,3,5-triphenyltetrazolium chloride – water – chloroform system)[137], and $\log \beta = 9.04$, $\log K_D = 1.11$ and $\log K_{ex} = 11.15$ (for the Ge(IV) – 4-NC – 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide – water – chloroform system).[136]

5. 13. Complexes of Mg

Häkkinen[114–116] investigated potentiometrically the complex formation in aqueous solutions between Mg^{2+} and NDCs (H_2L: 3-NC, 4-NC and 3,5-DNC). He detected the complexes MgL and MgL_2^{2-} in all studied systems. Their stability constants were calculated to be $\log \beta_1 = 5.72$ and $\log \beta_2 = 9.77$ (for the system containing 3-NC)[115], $\log \beta_1 = 5.21$ and $\log \beta_2 = 8.85$ (for the system containing 4-NC)[114] and $\beta_1 = 4.53$ and $\log \beta_2 = 7.71$ (for the system containing 3,5-NC)[116]. Another complex, Mg(OH)L, with log $\beta = 5.8$ was found in the system containing 3,5-DNC.[116] All measurements were carried out at 25 °C and an ionic strength of 0.1(KCl).

5. 14. Complexes of Mn

Häkkinen[65] showed that Mn(II) forms three complexes with 3-NC in aqueous solutions (MnL, MnL_2^{2-} and MnHL). Their stability constants were calculated to be log $\beta_1 = 7.22$, log $\beta_2 = 12.5$ and log $\beta_{1h} = 13.3$ (25 °C, 0.1 mol/l KCl ionic strength).

The interaction between Mn(II) and 4-NC has been investigated by several authors.[75,118,119,140] Species with 1:1 and 1:2 Mn(II) to 4-NC molar ratios were detected by Murakami et al.[75] and Häkkinen.[118] They reported the following values of their stability constants: log $\beta_1 = 6.51$ and log $\beta_2 = 11.25$ (30 °C, 0.10 mol/l KNO_3 ionic strength)[75], and log $\beta_1 = 6.83$ and log $\beta_2 = 11.72$ (25 °C, 0.1 mol/l KCl ionic strength).[118] Tyson and Martell[119] showed that 1:1-complex species have catalytic effect on the oxidation of catechol to o-benzoquinone and 3,5-di-tert-butylcatechol (3,5-DTBP) to corresponding o-quinones. In order to throw more light on the differences in 4-NC binding to some enzymes, such as extradiol-cleaving catechol dioxygenases, Reynolds et al. synthesized and compared monoanionic and dianionic 4-NC complexes of Mn(II) and Fe(II).[140]

5. 15. Complexes of Mo

Mo(VI) is known to form colored 1:1 and 1:2 complex species with 4-NC (H_2L), which could be represented with the following formulae[141,142]: MoO_2L, $MoO(OH)L^+$, $MoO_2(OH)_2L^{2-}$ and $MoO_2L_2^{2-}$. The formation constant of $MoO_2L_2^{2-}$, which is the complex of analytical importance, was found to be log $\beta_2 = 22.8 \pm 0.8$ at 25 °C and 0.100 mol/l KCl ionic strength.[142] Several ion-association complexes with participation of Mo(VI) – 4-NC anionic chelates and tetrazolium cations were studied in solutions[143–147] and solid state.[63] These complexes are slightly soluble in water and easily extracted into organic solvents. Equilibrium constants which characterize the extraction process (extraction constant – K_{ex}, distribution constant – K_D and association constant – β) were calculated by Dimitrov et al.[143–147] Their values are included in Table 8. Molar absorptivity coefficients of these complexes are in the range $(1.94–2.41) \times 10^4$ L mol^{-1} cm^{-1} and they were successfully applied for LLE-spectrophotometric determination of Mo(VI) in ferrous metallurgy products (steels, ferromolybdenum). A more sensitive flotation-spectrophotometric procedure ($\varepsilon = 2.1 \times 10^5$ L mol^{-1} cm^{-1}) was developed for the determination of Mo(VI) in biological materials.[148] It is based on the formation of an ion-associate between the 3,5-DNC – Mo(VI) anionic chelate and rhodamine B: $(RB^+)_2[MoO_2(3,5\text{-}DNC)_2]$. The procedure was reported to be specific after a preliminary separation of molybdenum by its extraction as the α-benzoinoxime complex from 2 mol/l HCl.[148,149]

Preparation and spectroscopic characterization were reported for monooxomolybdenum(VI) complex, MoO(4-NC)(DEASNBH), where $DEASNBH^{2-}$ = dianion of *N*-4-diethylaminosalicylidene-*N*'-4-nitrobenzoyl hydrazine. The compound was prepared by replacement of an oxo group on MoO_2(DEASNBH) with 4-NC. The complex exhibits a Mo = O stretching vibration ($\nu_{Mo=O}$) at 935–938 cm^{-1} and a series of five absorptions in the UV–Vis region including a long wave-length band at 655–658 nm which is attributed to 4-NC → Mo charge transfer.[150]

5. 16. Complexes of Nb

Nb(V) forms colored anionic species with NDCs (4-NC and 3,5-DNC) with an Nb(V)-to-NDC ratio of 1:2 or 1:3, which can be associated with heavy organic cations such as tetrazolium cations[151–157] and basic dyes.[149,158] Several slightly soluble in water ternary or quaternary complexes with analytical potential were obtained. They were extracted into organic solvents[151–157] or floated with cyclohexane.[149,158] The highest sensitivity ($\varepsilon_{555} = 2.1 \times 10^5$ L mol^{-1} cm^{-1}) was achieved in the last case. The following formula of the floated compound[158] was suggested:

Table 8. Equilibrium constants (extraction constant – K_{ex}, distribution constant – K_D and association constant – β) for LLE-systems involving Mo(VI), 4-NC (H_2L) and tetrazolium halides.

Suggested formula	Organic solvent	Equilibrium constants log K_{ex}	log K_D	log β	Ref.
$(MTT^+)_2[MoO_2L_2]^{2-}$	$CHCl_3$	9.6	1.12	8.5	146
$(TT^+)[MoO_2(OH)L_2]^-$	$CHCl_3$	5.2	0.88	4.3	143
$(INT^+)_2[MoO_2L_2]^{2-}$	$C_2H_4Cl_2$	10.0	0.47	9.5	145
$(TV^+)_2[MoO_2L_2]^{2-}$	$C_2H_4Cl_2$	8.5	1.75	6.7	144
$(BT^{2+})[MoO_2L_2]^{2-}$	$C_2H_4Cl_2$	5.4	–	–	147

Abbreviations: MTT^+ – 3-(4,5-Dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium; TT^+ – 2,3,5-Triphenyl-2H-tetrazolium; INT^+ – 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium; TV^+ – 3-(2-Naphtyl)-2,5-diphenyl-2H-tetrazolium; BT^{2+} – 3,3'-[3,3'-Dimetoxy(1,1'-biphenyl)-4,4'-diyl]-bis[2,5-diphenyl-2H-tetrazolium]

Table 9. Equilibrium constants (extraction constant – K_{ex}, distribution constant – K_D and association constant – β) for LLE-systems involving Nb(V), NDC (4-NC, 3,5-DNC) and tetrazolium halides

Suggested formula	Organic solvent	Equilibrium constants log K_{ex}	log K_D	log β	Ref.
$(TT^+)[NbO(4\text{-}NC)_2]^-$	$CHCl_3$	3.25	–	–	151
$(INT^+)[NbO(4\text{-}NC)_2]^-$	$C_2H_4Cl_2$	3.71	0.73	3.12	152
$(TV^+)[NbO(4\text{-}NC)_2]^-$	$C_2H_4Cl_2$	4.53	1.61	3.01	153,154
$(MTT^+)_3[NbO(4\text{-}NC)_3]^{3-}$	$CHCl_3$	14.0	0.82	13.2	157
$(BT^{2+})_3[NbO(4\text{-}NC)_3]_2^{3-}$	$CHCl_3$	8.3	0.54	7.8	156
$(TT^+)_2[NbO(OH)(3,5\text{-}DNC)_2]^{2-}$	$CHCl_3$	9.9	1.02	8.9	155,156

Abbreviations: TT^+ – 2,3,5-Triphenyl-2H-tetrazolium; INT^+ – 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium; TV^+ – 3-(2-Naphtyl)-2,5-diphenyl-2H-tetrazolium; MTT^+ – 3-(4,5-Dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium; BT^{2+} – 3,3'-[3,3'-Dimetoxy(1,1'-biphenyl)-4,4'-diyl]-bis[2,5-diphenyl-2H-tetrazolium]

$(RB^+)_4[(NbO)_2C_2O_4(3,5\text{-}DNC)_2]$ (where RB means rhodamine B). A procedure for the determination of Nb(V) in geological samples based on this complex was described.[158]

The molar absorptivity coefficients for the complexes with participation of tetrazolium cations[154–157] are lower and may vary significantly (from $\varepsilon = 1.59 \times 10^4$ to $\varepsilon = 5.6 \times 10^4$ L mol^{-1} cm^{-1}). The most sensitive procedures are based on the complexes with formulae $(MTT^+)_3[NbO(4\text{-}NC)_3]$ and $(BT^{2+})_3[NbO(4\text{-}NC)_3]_2$, where MTT^+ and BT^{2+} are the cations which derive from 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide[157] and 3,3'-[3,3'-dimetoxy(1,1'-biphenyl)-4,4'-diyl]-bis[2,5-diphenyl-2H-tetrazolium] chloride[156], respectively. The 4-NC-to-Nb molar ratio in these complexes (3:1) is higher than that reported for other complexes with similar reagents (2:1) (Table 9). This is the key reason for the 2-3-fold higher molar absorptivity observed.[156,157] Another reason (for the first complex only) is the ability of MTT^+ to absorb light in the same spectral range where $[NbO(4\text{-}NC)_3]^{3-}$ absorbs.[157] Some equilibrium constants, which characterize the extraction of tetrazolium ion-association complexes, are shown in Table 9.

5. 17. Complexes of Ni

The complex formation between Ni^{2+} and the following NDCs was investigated in aqueous solutions: 3-NC[104], 4-NC[75,118] or 3,5-DNC.[81] Complexes with formulae NiL, NiL_2^{2-} and NiL_2^{4-} were detected potentiometrically. The values of their stability constants are shown in Table 10.

Table 10. Complexes of Ni(II) with NDCs (H_2L: 3-NC, 4-NC, 3,5-DNC) in aqueous solutions and their formation constants obtained potentiometrically

Complexes		3-NC	4-NC	3,5-DNC
[NiL]	$\log\beta_1 =$	8.12[a] [104]	7.2[a] [118], 7.82[b] [75]	6.84[a] [81]
$[NiL_2]^2$	$\log\beta_2 =$	13.9[a] [104]	13.2[a] [118], 13.9[b] [75]	11.94[a] [81]
$[NiL_3]^4$	$\log\beta_3 =$	17.4[a] [104]	16.9[b] [79]	15.3[a] [81]

a – at 25 °C and 0.1 mol/L ionic strength (KCl)
b – at 30 °C and 0.10 mol/L ionic strength (KNO_3)

5. 18. Complexes of Rare Earth Elements

The complex formation between rare earth ions RE(III) and NDCs (4-NC[69,70,159] and 3,5-DNC[160]) has been studied by potentiometry[69,70,159] and/or spectrophotometry.[69,159,160] Bhuyan and Dubey[70] determined some RE(III) – 4-NC formation constants at 25 °C and an ionic strength of 0.1, 0.15 and 0.2 mol/L (KNO_3). Their thermodynamic stability order was reported to be La(III) < Ce(III) ≅ Pr(III) < Nd(III) < Sm(III) < Gd(III) < Y(III) < Tb(III) < Dy(III) < Ho(III). The complexes of Eu(III) and Lu(III) with the same reagent (4-NC) were investigated by Zhu et al.[69] In contrast to the complexes of catechol, which have RE(III)-to-L ratios 1:1, 1:2 or 1:3 (at pH = 8.0, 10.0, and 12.0, respectively), the complexes of 4-NC contain only 1.5 catechol groups per Eu(III) and Lu(III).[69] 4-NC complexes of Sc(III) and Y(III) were investigated by Tűrkel et al.[159] The following stability constants were reported at 25 °C and ionic strength 0.1 mol/L KNO_3 (for the complexes of Sc) or $NaClO_4$ (for the complexes of Y): $\log \beta_1 = 13.58$ (ScL^+), $\log \beta_2 = 27.35$ (ScL_2^-), $\log \beta_3 = 40.14$ (ScL_3^{3-}), $\log \beta_1 = 9.83$ (YL^+), $\log \beta_2 = 18.39$ (YL_2^-) and $\log \beta_{3h} = 24.39$ (YHL_3^{2-}).

The interaction in water-organic solvent medium between RE(III), 3,5-DNC and some basic dyes (methylene blue, Nile blue, malachite green, brilliant green, methyl

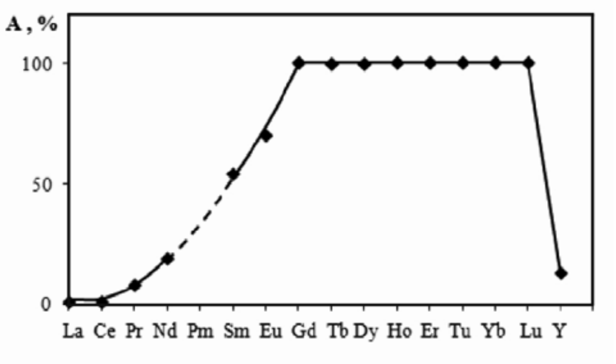


Figure 1. Relative absorbance ($A_{RE(III)–3,5\text{-}DNC–RB} \times 100/A_{Dy(III)–3,5\text{-}DNC–RB}$) vs. the nature of RE.[160] $C_{RE(III)} = 2 \times 10^{-5}$ mol/L, $C_{3,5\text{-}DNC} = 1 \times 10^{-4}$ mol/L, $C_{RB} = 5 \times 10^{-5}$ mol/L, pH = 6.3, λ = 553–565.

violet, rhodamine B and rhodamine G) were investigated by Poluektov et al.[160] The best extraction-spectrophotometric characteristics were obtained with rhodamine B and mixed organic solvent (benzene:izobutanol (9:1)). The molar ratio between the components was found to be RE : 3,5-DNC : RB = 1 : 4 : 1 {suggested formula $(RB^+)[RE(HL)_4]$}. The relative absorbance at λ = 553–565 nm ($A_{RE(III)-3,5-DNC-RB} \times 100/A_{Dy(III)-3,5-DNC-RB}$) vs. the nature of RE is plotted in Fig. 1. It can be seen that La(III) and some other RE do not interfere at the defined optimum conditions on the determination of Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III) and Lu(III). On this basis an LLE-spectrophotometric procedure for determination of Gd(III) in the presence of La(III) was developed.[160]

5. 19. Complexes of Si

Quantitative data for the reaction $3H_2L + Si(OH)_4 \leftrightarrow SiL_3^{2-} + 4H_2O$ (where H_2L is 4-NC, 3,4-DNC, catechol, or 4,5-dichlorocatechol) in aqueous solution were obtained by ^1H and ^{29}Si NMR spectroscopy.[161] Mixed complexes containing catechol and 4-NC or catechol and 4,5-dichlorocatechol were obtained as well.[161]

Riedel and Spange[89] prepared several silicates containing 4-NC ligands in order to investigate their solvatochromism: sodium tris(4-nitrobenzene-1,2-diolato)silicate, tetra-n-butylammonium tris(4-nitrobenzene-1,2-diolato)silkate, pyrrolidinium tris(4-nitrobenzene-1,2-diolato)silicate, (3-amino-1-propyl)-bis(4-nitrobenzene-1,2-diolato)silicate and (N,N-diethyl-3-amino-1-propyl)-bis(4-nitrobenzene-1,2-diolato)silicate. The authors showed that the solvent-induced UV/Vis band shift of the negatively charged moiety of all solvatochromic dyes studied is mainly a function of the hydrogen-bond donor strength and the dipolarity/polarizability of the solvent. Hydrogen-bond donor solvents cause a hypsochromic shift of the UV/Vis band due to specific solvation of the anion site. Inversely, increasing dipolarity/polarizability of the solvent induces a bathochromic shift of the UV/Vis absorption band.[89]

5. 20. Complexes of Sn

The reaction between molar equivalents of dibutyltin(IV) oxide and some catechol derivatives (including 4-NC) were reported to give monochelated dibutyltin(IV) catecholates of the general formula Bu_2SnL.[162] Results of a lethality bioassay on the brine shrimp indicated that all the complexes have biological activity.[162]

The complex formation in aqueous medium between Sn(IV) and 3,5-DNC was investigated by Nazarenko et al.[90] Only one complex, $H_2[SnL_3]$, is formed in slightly acidic solution (pH_{opt} = 2), independent from the H_2L-to-Sn(IV) concentration ratio. The absorption maximum of the complex is situated at 360 nm, but a more convenient wavelength for the measurements was λ = 400 nm. At this wavelength the blank absorbed insignificantly and the molar absorptivity was satisfactory ($\varepsilon_{400} = 8.6 \times 10^3$ L mol^{-1} cm^{-1}).[90]

A much more sensitive procedure for the determination of Sn(IV) ($\varepsilon_{630} = 1.75 \times 10^5$ L mol^{-1} cm^{-1}) was proposed by the same authors.[90,163] The procedure is based on the extraction of a ternary complex with 3,5-DNC (H_2L) and brilliant green, $(BG^+)_2[SnL_3]$, into CCl_4. The following other combinations of basic dye and organic solvent were tested during the optimization: methyl violet – C_6H_6, malachite green – CCl_4, Nile blue A – C_6H_6, methylene blue – $CHCl_3$, basic blue – C_6H_6, phenosafranine – $CHCl_3$, rhodamine B – C_6H_6, and rhodamine 6G – C_6H_6. However, the molar absorptivity in all mentioned cases was smaller (up to 1.3×10^5 L mol^{-1} cm^{-1}).[90]

5. 21. Complexes of Sr

The complex formation in the aqueous system Sr^{2+} – NDC, where NDCs (H_2L) are 3-NC,[115] 4-NC[114] and 3,5-DNC[116] was investigated potentiometrically at 25 °C and 0.1 mol/L ionic strength (KCl) by Häkkinen. All mentioned reagents form complexes with a general formula SrL. Their formation constants were calculated to be log β_1 = 3.14,[115] 2.81[114] and 2.28,[116] respectively. 4-NC and 3,5-DNC form complexes with a formula SrL_2^{2-} as well. The formation constants for these complexes were calculated to be log β_2 = 5.18[114] and 4.54,[116] respectively.

5. 22. Complexes of Tc

Tetra-n-butylammonium bis(4-nitro-1,2-benzenediolato)oxotechnetate(V) was synthesized and its structure reported by Rochon et al.[164] The geometry around the Tc atom is square pyramidal with a short Tc–O(oxo) bond in the apical position. The Tc atom lies out of the plane of the four diolato O atoms. The nitro groups are in the same planes as the catecholato ligands. The NO_2 of one ligand is disordered.

5. 23. Complexes of Tl

Intensively colored ternary ion-association complexes with composition 1:2:1 are formed in the system Tl(III) – catechol derivative – basic dye.[165,166] The complexes with NDCs were found less appropriate for analytical applications than the analogical complexes with tetrabromocatechol or catechol. The last mentioned reagent was applied for the determination of Tl(III) in alkaline salts.[165]

5. 24. Complexes of Ti

Complex formation in LLE systems containing Ti(IV), catechol derivative (3,5-DNC, tetrabromocatechol and tetrachlorocatechol) and basic dye (methylene blue, basic blue, gallocianine, Nile blue A, phenosafranine, brilliant green, Victoria blue 4R, malachite green, methyl violet) was examined by Nazarenko et al.[167] The complex with 3,5-DNC and brilliant green, $(BG)_2[TiOL_2]$, was reported to have the highest molar absorptivity (ε_{640} = 2 × 10^5 L mol^{-1} cm^{-1} in CCl_4). However, tetrachlorocatechol was chosen for the development of a procedure for Ti(IV) determination in real samples.[167]

Two ternary ion-association complexes of Ti(IV)-4-NC anionic chelate, $[TiOL_2]^{2-}$, and tetrazolium cations with general formula $(TS^+)_2[TiOL_2]$ were studied by Kostova et al.[168] The key equilibrium constants characterizing their extraction from water into chloroform were calculated: log K_{ex} = 7.4, log β = 6.6 and log K_D = 0.74 {for the complex with 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium}, and log K_{ex} = 12.1, log β = 10.0 and log K_D = 1.9 {for the complex with 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium}. The associate with the second cation has better characteristics and was used for LLE determination of Ti in aluminium alloys (Table 3).[168]

Strong adsorption of 4-NC onto Ti(IV)-bearing surfaces was observed by Vasudevan and Stone.[107] They determined the stoichiometry of surface complex formation and the intrinsic equilibrium constants for adsorption onto three Ti(IV) oxides. Araujo et al.[169] compared the stability of the surface complexes of several ligands (4-NC, 2,3-dihydroxynaphtalene, catechol, gallic acid and 4-chlorocatechol) with titanium dioxide in aqueous suspensions. They found that 4-NC and 2,3-dihydroxynaphtalene form the most stable complexes, probably because of the solvation contribution to the overall Gibbs adsorption energy.[169]

5. 25. Complexes of U

The complex formation in aqueous solutions between UO_2^{2+} and 4-NC (H_2L) was investigated potentiometrically by Bartušek.[82] UO_2L , $UO_2L_2^{2-}$ and $UO_2L_2H^-$ were detected in the system at different conditions. The stability constants of the first two species were calculated to be $\log\beta_1$ = 12.9 and $\log\beta_2$ = 22.7, respectively. The acidic dissociation constant of $UO_2L_2H^-$ was found as well (pK = 4.97). All measurements were carried out at 20 °C and an ionic strength of 0.1 mol/l (KNO_3).

5. 26. Complexes of V

Yellow species are formed at mixing aqueous solutions of V(IV) or V(V) and NDCs (4-NC, 3,4-DNC or 3,5-DNC).[170–174] The absorption maximum of the complex of V(V) and 3,5-DNC is at 428 nm (pH = 1–3)[171]. The complexes of V(V) or V(IV) with 4-NC have absorption maxima at 405–410 nm in the pH region between 2 and 5.[172–174] The molar V(IV)-to-4-NC ratio was determined to be 1:1.[173] The complex is nonextractable in chloroform, but well extractable into n-butanol.[174]

Several ternary ion-associated complexes containing the mentioned NDCs and organophilic cations (deriving from tetrazolium salts,[172–183] basic dyes[171,184] and dipheniylguanidinium chloride[170]) have been characterized. The complexes of V(V), 3,5-DNC and basic dyes were investigated by Marczenko and Lobinski.[171,184] The complexes with brilliant green, $(BG^+)_2[VO(OH)L_2]$, and rhodamine B, $(RB^+)_2[VO(OH)L_2]$, have the highest analytical potential. The first one was utilized for LLE-spectrophotometric determination of traces of vanadium (about 10^{-5}%) in alums and the second one for flotation-spectrophotometric determination of vanadium in vegetables.[184]

The complexes of 4-NC and tetrazolium cations are also of analytical importance. They were applied for the determination of total vanadium in steels[172,179,183] and catalysts[183], as well as for vanadium(IV/V) speciation in synthetic mixtures and industrial samples with low Fe and Al content.[182] The speciation V(IV/V) analysis with 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium (MTT) is based on spectral differences at optimized reagent concentrations (Fig. 2). Some equilibrium constants, which characterize LLE of the tetrazolium ion-associated complexes, are presented in Table 11.

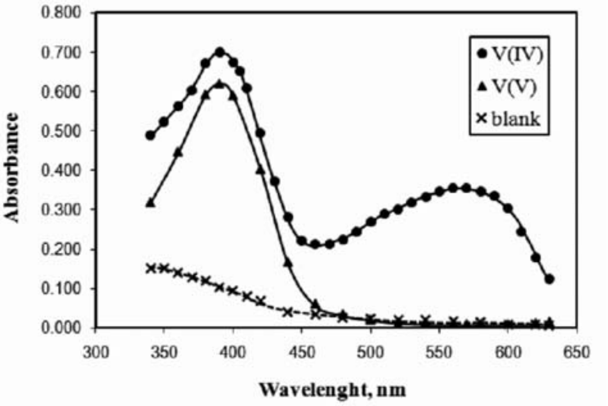


Figure 2. Spectra of the V(IV) – 4-NC – MTT complex, the V(V) – 4-NC – MTT complex and the blank (4-NC – MTT) in chloroform[182]. $C_{V(V)} = C_{V(IV)} = 2 \times 10^{-5}$ mol/L, $C_{4\text{-}NC} = 3.6 \times 10^{-5}$ mol/L, $C_{MTT} = 1.6 \times 10^{-4}$ mol/L, pH = 4.7, l = 1 cm

5. 27. Complexes of W

The complex formation in aqueous systems containing W(VI) and 3,5-DNC[185] or 4-NC[141] was investigated by Poluektova et al. and Natansohn et al., respectively. The complex with 3,5-DNC, $H_2[WO_2L_2]$, was recommended for determination of W(VI) (ε_{400} = 1 × 10^4 L mol^{-1} cm^{-1}). Its instability constant was calculated to be 1.8 × 10^{-21} (25 °C, I = 0.1 mol/L $NaNO_3$).[185]

Several ternary complexes with participation of W(VI) – 4-NC or W(VI) – 3,5-DNC anionic chelates and bulky organic cations have been studied.[186–188] These complexes are slightly soluble in water and easily extractable into organic solvents ($CHCl_3$). Their molar absorptivity coefficients are in the range from ε_{400} = 1.3 × 10^4 L mol^{-1} cm^{-1} (for the complex with antipyrine[186]) to 2.8 ×

Table 11. Equilibrium constants (extraction constant – K_{ex}, distribution constant – K_D and association constant – β) for LLE-systems involving V(IV) or V(V), 4-NC (H_2L) and tetrazolium salts.

Suggested formula	Organic	Equilibrium constants			Ref.
	solvent	log K_{ex}	log K_D	log β	
$(TT^+)_2[VOL_2]^{2-}$	$CHCl_3$	10.4	1.0	9.4	177
$(TT^+)_3[VOL_3]^{3-}$	$CHCl_3$	12.1	1.10	11.0	177
$(INT^+)_2[VOL_2]^{2-}$	$CHCl_3$	10.6	1.4	9.2	180
$(INT^+)_3[VO_2L_2]^{3-}$	$CHCl_3$	–	0.39	–	172,173
$(NT^{2+})_3[VO_2L_2]_2^{3-}$	$CHCl_3$+n-BuOH (7:3)	–	–	8.9	178
$(MTT^+)_2[VO_2L_2]^{2-}$	$CHCl_3$	12.9	1.9	11.0	181
$(MTT^+)_3[VO_2L_2]^{3-}$	$CHCl_3$	19.2	1.62	17.6	183

Abbreviations: TT^+ – 2,3,5-triphenyl-2H-tetrazolium; INT^+ – 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium; MTT^+ – 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium

Table 12. Equilibrium constants (extraction constant – K_{ex}, distribution constant – K_D and association constant – β) for LLE-systems involving W(VI), NDC (4-NC or 3,5-DNC) and tetrazolium salts.

Suggested formula	Organic	Equilibrium constants			Ref.
	solvent	log K_{ex}	log K_D	log β	
$(TT^+)_2[WO_2(NC)_2]^{2-}$	$CHCl_3$	10.3	1.05	9.2	187
$(MTT^+)_2[WO_2(NC)_2]^{2-}$	$CHCl_3$	10.3	1.03	9.3	188
$(TV^+)_2[WO_2(NC)_2]^{2-}$	$CHCl_3$	10.4	1.56	8.9	187
$(TT^+)[WO(OH)(DNC)_2]^-$	$CHCl_3$	10.6	1.06	9.6	187

Abbreviations: TT^+ – 2,3,5-triphenyl-2H-tetrazolium; MTT^+ – 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium; TV^+ – 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium

10^4 L mol^{-1} cm^{-1} (for the complex with thiazolylblue tetrazolium[188]). Some of them were successfully applied for the determination of W(VI) in ferrous metallurgy products.[187,188] Equilibrium constants (extraction constant – K_{ex}, distribution constant – K_D and association constant – β), which characterize the extraction of tetrazolium ion-association complexes were calculated by Dimitrov et al.[187,188] Their values are given in Table 12.

5. 28. Complexes of Zn

The complex formation in the aqueous systems Zn^{2+} – 3-NC, Zn^{2+} – 4-NC and Zn^{2+} – 3,5-DNC was investigated potentiometrically at 25 °C and an ionic strength of 0.1 mol/l (KCl) by Häkkinen.[65,66,81] Complexes with general formulae ZnL and ZnL_2^{2-} were detected in all systems. Their stability constants are as follows: $\log\beta_1 = 8.64$ and $\log\beta_2 = 15.80$ (for the complexes with 3-NC)[65], $\log\beta_1 = 8.25$ and $\log\beta_2 = 14.85$ (for the complexes with 4-NC)[66], and $\log\beta_1 = 6.92$ and $\log\beta_2 = 12.79$ (for the complexes with 3,5-DNC).[81]

5. 29. Complexes of Zr

Zr(IV) forms only one complex with 3,5-DNC in acidic aqueous solutions (optimum acidity 0.1–1.0 mol/L HCl).[189] This complex is electroneutral (suggested formula $[Zr(OH)_2L]$), but not extractable into organic solvents. Its molar absorptivity was calculated to be $\varepsilon_{max} = 6.1 \times 10^3$ L mol^{-1} cm^{-1} at $\lambda_{max} = 328.5$ nm. In the presence of pyrazolone derivatives (antipyrin or diantipyrylmethane) ternary compexes with 1:2 Zr-to-3,5-DNC ratio are formed. The molar absorptivities of these complexes are higher and bathochromic shifts are observed in their spectra: $\varepsilon_{420} = 1.5 \times 10^4$ L mol^{-1} cm^{-1} for the complex of antipyrine $(Ant^+)_2[Zr(OH)_2L_2]^2$ and $\varepsilon_{410} = 2.06 \times 10^4$ L mol^{-1} cm^{-1} for the complex with diantipyrylmethane $DAM^{2+}[Zr(OH)_2L_2]^2$. The complex with DAM has better characteristics, however $(Ant^+)_2[Zr(OH)_2L_2]^2$ was used for LLE spectrophotometric analysis of real samples (Table 3). The relative standard deviation was calculated to be RSD = 1.2%.[189]

6. Other Applications

Except for the above-mentioned application as analytical reagents, simple NDCs are widely used as model reagents for elucidation of various environmental[86,142] and physiological[190,191] processes. Some NDCs were disclosed as important inhibitors,[191–196] antioxidants,[28,194,195] selectin modulating compounds[197] and precursors for a wide range of syntheses.[198–202] Derivatives of 3-NC with a bulky substituent group in position 5 are well known therapeutic agents.[194–196,203,204] The most important representatives of this class of compounds are nitecapone, entacapone and tolcapone {their systematic names are (3,4-dihydroxy-5-nitrobenzylidene)-2,4-pentanedione; (2*E*)-2-cyano-3-(3,4-dihydroxy-5-nitrophenyl)-*N*,*N*-diethylprop-2-enamide; and (3,4-dihydroxy-5-nitrophenyl)(4-methylphenyl)methanone, respectively}. Nitecapone exerts cardioprotective[205] and gastroprotective effects,[195] while entacapone may protect from angiotensin II-induced inflammation and renal injury.[206] As a highly effective inhibitor of catechol-O-methyltransferase (COMT) entacapone is used for the treatment of Parkinson's disease patients.[204]

7. Conclusion

NDCs are widely used in various fields including analytical and environmental chemistry, biochemistry and pharmacology. They form complexes with many metal ions. The stability order among the simple NDCs used as ligands in binary complexes follows the sequence: 3,5-DNC<4-NC<3-NC. The most important participants in this row, however, are 4-NC and 3,5-DNC. Additional investigations on complexes of these compounds, as well as on some 5-substituted derivatives of 3-NC, are worth performing. Further experiments may significantly expand the sphere of their applications.

8. Acknowledgments

The author would like to thank the Research Fund of the Plovdiv University for its long-time support (Grant Nos H13-2005, MU-11-2008, RNI09-HF-002, RS09-HF-010 and NI2011-HF-007).

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Povzetek

Podan je pregled nitro derivatov katehola (NDCs) s posebnim poudarkom na njihovih kompleksih in aplikacijah. Predstavljeni so binarni, terciarni in kvarterni NDC kompleksi z več kot 40 elementi (aluminij, arzen, bor, berilij, kalcij, kobalt, baker, železo, galij, germanij, magnezij, mangan, molibden, niobij, redke zemeljske kovine, silicij, kositer, stroncij, tehnecij, talij, titan, uran, vanadij, volfram, cink in cirkonij), njihova uporaba v analitiki in ključne karakteristike razvitih analiznih postopkov.