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A review on the complex forming ability of O-O′ type ligands with transition metals: introducing 2,3-dihydroxynaphthalene as a potential analytical reagent

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Abstract

O-O′ type organic compounds and their derivatives are known to form a host of complexes in solutions, and many of them have been isolated in solid forms and characterized by physicochemical techniques, including X-ray crystallography. Some of the complexes have been shown to have biological significance. Many of the complexes of ortho-dihydroxybenzene and -naphthalene formed in solution with metal ions, particularly transition metals, display distinct colors under different reaction conditions. These colored complexes are often suitable for spectrophotometric determinations of the metals. Comparative studies carried out on a host of complexes of metal ions with different ortho-dihydroxybenzenes and -naphthalenes reveal that the color complexes formed of the latter are invariably more sensitive than those formed of the former because of ring size and extended conjugations. Among the ortho-dihydroxynaphthalenes studied, the one having oxygen atoms at positions 2 and 3 of the ring [2,3-dihydroxynaphthalene (2,3-H_2ND)] has high propensity to form colored complexes with a host of metal ions suitable for liquid-liquid extraction under different reaction conditions. A survey of the literature reveals that except for a few scarce reports, the analytical potential of this ligand, although it had in the past been extensively used in the synthesis and structural assessment of numerous complexes with different metal ions, has not been explored thoroughly until recently studied in detail in the authors' laboratory. This paper presents a non-exhaustive review on the complex forming ability of 2,3-H_2ND vis-à-vis those of its other counterparts, with special reference to its analytical applications.

Keywords: complex forming ability; 2,3-dihydroxynaphthalene O-O′ type organic compounds; review.

O-O′ type ligands including 2,3-H_2ND in the synthesis of metal complexes and their biological significance

Complexes derived from ligands having O-O′ type functional groups present on aromatic rings such as catechol, 2,3-H_2ND, 3,4-dihydroxybenzoic acid and 3(3,4-dihydroxyphenyl) propionic acid were charac-terized in solutions as well as solids (Salmonsen et al. 1984). Metal catechol complexes often exhibit unusual electronic effects owing to the ability of both the ligand and metal ion to undergo electronic transfer (Raymond et al. 1980, Lynch et al. 1981, Pierpont and Buchanon 1981, Jones et al. 1982) and are of major interest because such systems present models for the biological transport of iron (Raymond et al. 1980, Jones et al. 1982) for some enzymes and for the primary photoelectron donor-acceptor center in bacterial photosynthesis (Lynch et al. 1982). They can also serve as models for the metal ion interactions with ascorbate in the udenfriend system and ascorbate oxidase (Pell et al. unpublished results, Seib and Tolbert 1982). Species containing catechol moiety have long been known to form complexes with iron (Secundii 1684) and other metals (Pierpont and Buchanon 1981). It has also been reported that catechol and substituted catechols bind strongly to osmium (Hursthouse et al. 1978, Nielson and Griffith 1978), molybdenum and tungsten (Stabler 1986) via the deprotonated O-O′ sites (Hursthouse et al. 1978, Nielson and Griffith 1978, Griffith et al. 1986). Catecholamines are biogenic amines which function as neurotransmitters in the brain and nervous system of mammals (Stabler 1986).

Catecholamines such as adrenaline, noradrenaline, dopamine, DOPA (3,4-dihydroxyphenylalanine) and isoproterenol, all having O-O′ sites form complexes (Griffith et al. 1987) with Cu, Ni, Co, Os, U, Mo, W, Pt, Pd, etc. Similar compounds such as tropolone (Griffith et al. 1987) (Htrop) and maltol (Greaves and Griffith 1988) (Hmalt), 3-hydroxy-2-methyl pyran-4-one, ($C_6H_6O_3\cdot$) have been reported to form complexes with ruthenium, rhodium, palladium, platinum, molybdenum and uranium. Studies on the determination of stability constants of some metal ions in solution have also been carried out using different orthodihydroxy aromatic ligands such as catechol, 3,4-dihydroxytoluene, 1,2-dihydroxybenzene, 2,3-dihydroxytoluene, 1,2,3-trihydroxybenzene, 3,4-dihydroxybenzoic acid, 1,2-dihydroxy-4-chlorobenzene, 3,4-dihydroxybenzaldehyde, 1,2-dihydroxy-4-nitrobenzene, 3,4,5-trihydroxybenzoic acid and 2,3-H_2ND.

Among the above, 1,2-dihydroxybenzene(catechol) has been extensively studied. A series of complexes of molybdate ion (Weinland and Gaisser 1919, Weinland and Huthmann 1924, Fernandes 1925, Weinland and Babel 1925) were prepared with catecholate ligand. These compounds and the solution chemistry of Mo(VI)-catechol systems have gained a particular importance as a photometric analytical method for the determination of molybdenum (Seifter and Novic 1951, Soni and Bartusek 1971). In neutral solution, a red orange complex with a Mo:catechol ratio of 1:2 is formed, whereas at pH values below 2, a 1:1 complex is observed (Haight and Pargamian 1960).

Atovmyan et al. have characterized products of early synthetic reaction crystallographically and found them to contain the $MoO_2(Cat)_2^{2-}$ and $Mo_2O_5(Cat)_2^{2-}$ ions (Atovmyan et al. 1970, 1972). More recently, kinetic studies have been carried out on the molybdate-catechol system (Kustin and Kiu 1973) and the redox chemistry of molybdenum-catecholate complexes has been investigated in detail (Wilshire et al. 1979a,b, 1980). The interactions of scandium(III) and yttrium(III) ions with catechol, 4-nitrocatechol and 2,3-H_2ND-6-sulfonic acid were investigated in different metal ion:ligand mole ratios by potentiometry and spectrophotometry (Turkel et al. 1999). The stoichiometries of complexes were defined by Job's method.

In addition to the extensive studies carried out on the complexes of catechol and its derivatives in solid forms (synthesis and structural assessments) as well as in solutions (equilibrium studies and analytical applications), similar studies, although scarce, are, however, not unprecedented with the ligand 2,3-H_2ND.

Complexes of molybdenum, tungsten, osmium, uranium, palladium and platinum with this reagent have been synthesized, isolated in solid forms and characterized. One such complex, cis-$(NH_4)_2[Mo_2O_5(ND)_2]\cdot 2H_2O$ has been characterized by X-ray crystal structure (El-Hendaway et al. 1989) determination. Atom numbering of the compound 2,3-H_2ND is shown in Figure 1. The perspective views of the $[Mo_2O_5(ND)_2]^{2-}$ are shown in Figures 2 and 3. The isolated complexes are cis-$[Ru(NH_3)_4(ND)]Cl$ (Salmonsen et al. 1984), $Sn(ND)_2$ and $(Bu_4N)_2[Sn(ND)_3]$ (Soto et al. 1982), $(Et_3N)[Ph_3Sb(ND)Cl]$ (Holmes et al. 1987) and (pyH) $[PhSi(ND)_2]$ (Holmes et al. 1984) and bis (tri-n-butylammonium) tris (2,3-dihydroxynaphthalato) silicate (Suvitha et al. 2006). X-ray crystallographic studies were described for the latter three complexes.

In addition, some other boron (Lim et al. 2003) and ruthenium (Yang et al. 1997) complexes of 2,3-H_2ND are also known. Synthesis of 2,3-H_2ND derivatives of [3n] crown-n macrocycles has been reported (Yapar and Erk 2001). This was synthesized by the reaction of 2,3-H_2ND and polyglycoldihalides and studied for their cationic recognition properties using steady-state fluorescence spectroscopy. The association constants for the interaction of 2,3-naphthol (Griffith et al. 1986) crown-4,2,3-naphthol (Greaves and Griffith 1988) crown-5,2,3-naphthol (Weinland and Babel 1925) crown-6 with $LiClO_4$, $NaClO_4$, NaSCN and KSCN were measured in acetonitrile. Excellent correlation of spectroscopic, cationic charge radii and macro cycle backbone size data was found.

Recently, ternary complexes of titanium (Tinoco et al. 2008) with 2,3-H_2ND and bovine serum albumin were formed, and thorough biochemical studies were carried out (Figure 4). Serum albumin, the most abundant protein in human plasma (700 μM), binds diverse ligands at multiple sites. Although studies have shown that serum albumin binds hard metals in chelate form, few have explored the trafficking of these metals by this protein. Recent research demonstrated that serum albumin can play a pivotal role in the transport and bioactivity of titanium(IV) [Ti(IV)] complexes, including the anticancer drug candidate titanocene dichloride. A recent study explores this interaction further by using a stable Ti(IV) complex that presents a hydrophobic surface to the protein (Tinoco et al. 2008). Ti(IV) chelation by 2,3-H_2ND and 2,3-H_2ND-6-sulfonate affords water soluble complexes that protect Ti(IV) from hydrolysis at pH 7.4 and bind to bovine serum albumin. The solution and solid Ti(IV) coordination chemistry were explored by aqueous spectropotentiometric titrations and X-ray crystallography, respectively, and with complementary electrochemistry, mass spectrometry, and IR and NMR spectroscopies.

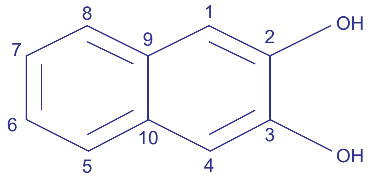

Figure 1 2,3-H_2ND with atom numbering scheme.

Analytical applications of 2,3-H_2ND

Probably because of the presence of two hydroxyl groups at positions 2 and 3 of the naphthalene ring, the reagent, 2,3-H_2ND, is having more delocalization of electron compared to catechol and chromotropic acid. Consequently, the color intensity of the complexes formed of transition elements with this ligand is always more, i.e., the sensitivity of reaction is generally much higher because of extended delocalization of electrons owing to increase in the ring size, a criterion for high sensitivity color reaction (Morton et al. 1993).

Organic compounds having oxygen containing functional groups at "ortho" position on benzene and naphthalene rings demonstrate strong complexing ability for transition elements. A review on "complexation of phenolic hydroxyl and its analytical consequences" is available in the literature (Sommer et al. 1966).

Catechol (Griffith et al. 1986) (1,2-dihydroxybenzene) and its derivatives such as tiron (Wakamatsu and Otomo 1972) (catechol disulfonic acid), 3,4-dihydroxybenzoic acid (Akhmad et al. 2007), 1,8-dihydroxynaphthalene and its derivatives such as 1,8-dihydroxynaphthalene-3,6-disulfonic acid (Sommer 1958, Biryuk and Nazarenko 1968) (chromotropic acid) and 2,3-H_2ND (Patrovsky 1970) are known to form color complexes with many metal ions. Similar ligands such as 1-nitroso-2-naphthol (Nichol 1953), different polyphenols (Sommer 1989), methoxyphenol (Tarafder et al. 1991) (guaiacol), etc., are also known to form color complexes with different metal ions.

The numerous azo derivatives of chromotropic acid (Brandt and Preiser 1953) (a well known reagent for titanium determination) such as arsenazo I and arsenazo III, thoron (Kuznetsov

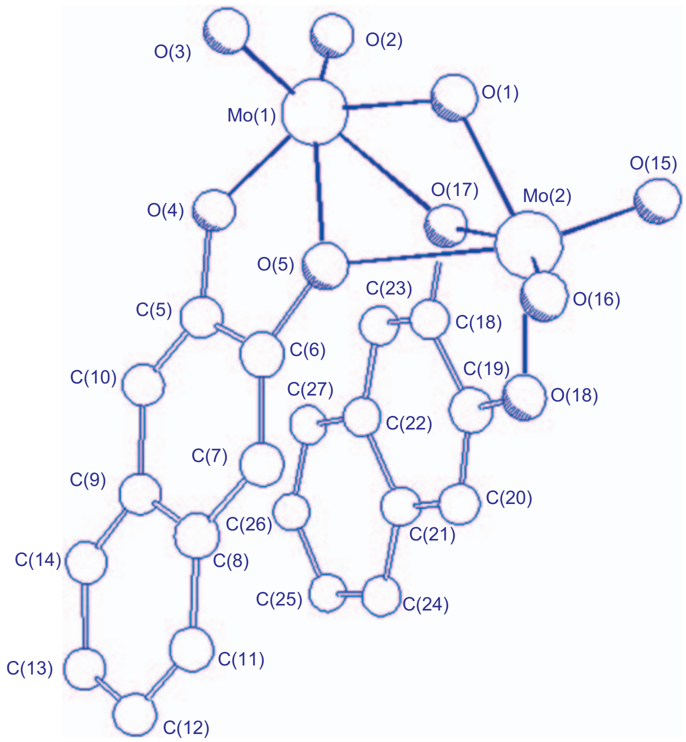

Figure 2 Perspective view of $[Mo_2O_5(ND)_2]^{2-}$ giving atom numbering (El-Hendaway, A. M. et al. *Polyhedron* **1989**, *8*, 519–525).

1941, 1944, 1959, Savvin 1959), chlorophosphonazo III, sulfochlorophenol S and sulfonitrophenol M (Savvin 1971) are potential complexing agents for the spectrophotometric determination of elements such as U, Th, Zr, Rare earths, etc. Similarly, O-O′ type dihydroxyarylazo compounds such as picramine epsilon (Dedkov and Kotov 1970), eriochrome black T (Harvey et al. 1953) and calmagite (Flaschka and Sawyer 1962) are well known complex forming analytical reagents. Even the complexing abilities of triphenylmethane reagents such as pyrocatechol violet (Biryuk and Ravitskaya 1970), eriochrome cyanine R (Malat 1961), chromeazurol S (Suk and Miket'ukova 1959), as well as xanthene reagents such as gallein (Antonovich et al. 1977), bromopyrogallol red (Antonovich et al. 1976) phenylfluorones (Antonovich et al. 1984) are attributed to the presence of O-O′ type functional groups on benzene or fused benzene rings.

Surprisingly, there are few complexes known of this readily available ligand. There are solution studies on its complexation with boron (Sato and Uchikawa 1980), molybdenum (Patrovsky 1970, Il'yasov et al. 1972, Soni and Nahata 1972, Natansohn et al. 1980, Usmanov and Novosadov 1982, Lekova et al. 2003), tungsten (Il'yasov et al. 1972, Natansohn et al. 1980, Usmanov and Novosadov 1982, Dimitrov and Alexandrov 1995, Gavazov et al. 2006), uranium (Bartusek 1967), iron, titanium (Patrovsky 1970, Il'yasov et al. 1972, Kostova et al. 2000), niobium (Aleksandrov et al. 1983) and vanadium (Patrovsky 1970, Simeonova et al. 2006, Lekova et al. 2007). Some researchers in the past have studied the reaction of boron with 2,3-H$_2$ND spectrophotometrically as well as fluorimetrically in the determination of boron.

The reaction of boron with 2,3-H$_2$ND followed by its extraction with crystal violet into organic solvent was the basis for sensitive determination of boron (Sato and Uchikawa 1980). In addition, the boron 2,3-H$_2$ND complex (Iwata et al. 2006) in aqueous solution was detected by measuring the fluorescence intensities (I_{ex}=300 nm, I_{em}=340 nm). The relative standard deviation at 20 ppb level was 2.6% (n=6). The limit of detection was 0.04 ppb.

Recently, 2,3-H$_2$ND has been used in the fluorimetric determination of manganese(II) [Mn(II)] by the catalytic oxidation of 2,3-H$_2$ND in the presence of ethylenediamine and hydrogen peroxide (Watanabe et al. 1995). The determination of Mn(II) which catalyzed a reaction between 2,3-H$_2$ND and ethylenediamine(en) has been investigated in the presence of hydrogen peroxide. A change in the reactants was detected by absorption and fluorimetric methods. Two types of intermediates, obtained from a mixture of 2,3-H$_2$ND, en and H_2O_2 were confirmed by changes in the fluorimetric spectra. One of them was used for the determination of Mn(II). The fluorescence intensity of the intermediate was measured at 500 nm with an excitation wavelength of 400 nm. The mechanism of the reaction between 2,3-H$_2$ND and en was discussed based on the change in the fluorescence spectra with the reaction time. The oxidation product, 2,3-naphthaquinone was reacted with en to form a quinoxaline derivative. The role of Mn(II) which forms the 2,3-H$_2$ND-Mn complex in the presence of H_2O_2 was only to accelerate the formation reaction of 2,3-naphthaquinone. Of late, the $[Fe(2,3\text{-}H_2ND)_n]$ complex has been used to estimate traces of iron in sea water by voltametry (Obata and Van den Berg 2001). Recently, a ternary complex

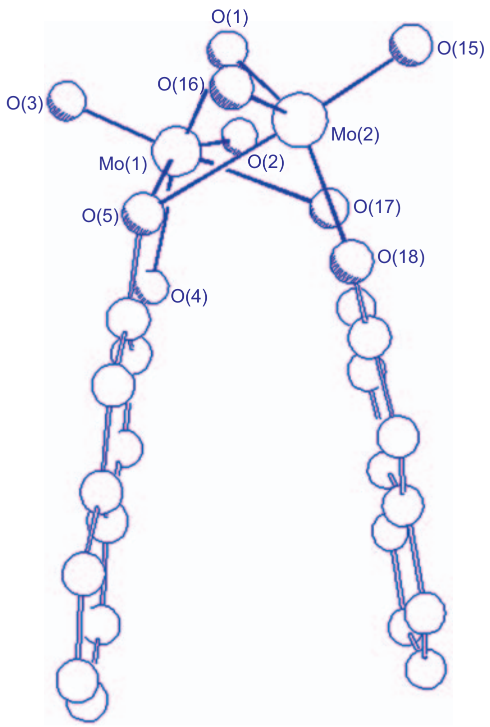

Figure 3 View of the $[Mo_2O_5(ND)_2]^{2-}$ anion approximately in the plane of the two naphthalene units (El-Hendaway, A. M. et al. *Polyhedron* **1989**, *8*, 519–525).

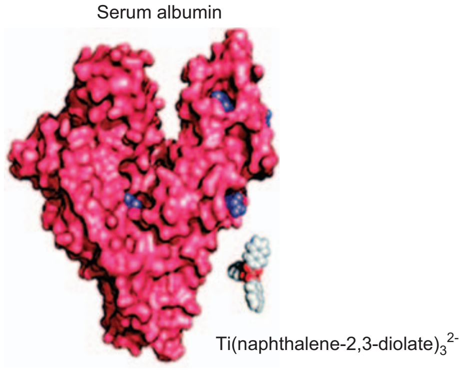

Figure 4 Ti(IV), 2.3-dihydroxynaphthalene and bovine serum albumin ternary complex (reprinted with permission from copyright © 2008, American Chemistry Society: Tinoco, A. D. et al. *Inorg. Chem.* **2008**, *47*, 8380–8390).

of boron with 2,3-H_2ND and insulin has been used in the flow injection analysis of boron (Iwata et al. 2007).

As has already been mentioned in the preceding section, many researchers have further derivatized a few such O'-dihydroxybenzenes or naphthalenes either by introducing the azo group such as 3,4-dihydroxyazobenzene, 2,3,4-trihydroxy-4-sulfoazobenzene and catechol and pyrogallol based azo compounds or by replacing one or both of the hydroxyl groups with functional groups such as nitroso(αnitroso-β naphthol), methoxy(guaiacol), amino(O-amino phenol) and carboxylic(salicylic acid) etc., with a view to increase the sensitivity (molar absorptivity) of the complexes by way of introducing extra auxochrome/conjugation.

Among the various di- and trihydroxybenzenes and toluenes as well as their sulfonic acid derivatives, catechol disulfonic acid (tiron) (Markzenko 1986) has been used extensively for the spectrophotometric determination of titanium, iron and few other transition elements. Similarly, ortho-dihydroxynaphthalene such as 2,3-H_2ND and 1,8-dihydroxynaphthalene, as well as their sulfonic acid derivatives have also been used for analytical purposes (Markzenko 1986). Although the sulfonic acid derivative of 1,8-dihydroxynaphthalene, which is also known as chromotropic acid is a well known analytical reagent for many elements such as Ti, V, Nb, etc., the analytical utility of the corresponding compound 2,3-H_2ND and its sulfonic acid derivative, although reported (Patrovsky 1970) to form color complexes with a host of elements such as V, Ti, Mo, Fe, Cu etc., has not been thoroughly explored until recently [Hrdlicka 1989, Tarafder et al. 1994, 2002, 2004, Tarafder and Sardana 2000, Mondal and Tarafder 2004, Gavazov et al. 2007, Minglu et al. 2007 (Table 1)]. It is pertinent to state that tiron is generally used for the sensitive estimation of titanium and iron but we have found that the reagent 2,3-H_2ND is far better than tiron for titanium and iron determination in terms of sensitivity and selectivity (the molar absorptivities of the titanium and iron complexes formed with this ligand are much higher compared with those formed with tiron). The enhanced sensitivity of metal complexes with this reagent prompted us to explore its analytical potential. A survey of the literature revealed that except for a few primary reports (Patrovsky 1970, Sato and Uchikawa 1980, Takayauagi and Yotsuyanagi 1994, Watanabe et al. 1995, Obata and Van den Berg 2001, Iwata et al. 2006, 2007), the potentiality of the reagent has not been explored further.

Recent developments on the analytical applications of 2,3-H_2ND

The presence of O-O′ type of non-innocent functional groups on the ortho position of the naphthalene ring attracted our attention to further probe into the analytical potentiality of this reagent. In doing so, we have investigated the complexation of elements such as Ti, Fe, Mo, V with this reagent in line with the findings of Patrovsky (Patrovsky 1970). As has already been discussed in the preceding section about the complex forming ability of the reagent, 2,3-H_2ND, we, in our laboratory have thoroughly investigated the analytical potential of this readily available reagent.

Unlike the report of Patrovsky (Patrovsky 1970) wherein iron (Fe^{3+}) was extracted with 2,3-H_2ND at pH 4.5–4.7 under the influence of the counter cation, tri-n-butylamine (Bu_3N) followed by its determination by measuring the absorbance of the ion associate at 510 nm, in the system developed in our laboratory, the neutral complex formed of 2,3-H_2ND and Fe^{3+} at pH 4–5 was exploited by measuring its absorbance either in aqueous solution or by extracting the same into ethyl acetate without any counter cation. Also, the reddish-orange anionic complex of 2,3-H_2ND with Fe^{3+} formed

Table 1 Analytical applications of 2,3-H_2ND.

Systems	Application in the field	λ_{max} (nm)	ε (l/mol/cm)	Beer's law range (mg/l)	Interference	Reference
B-2,3-H_2ND	Fluorimetry	$\lambda_{excit.}$=300 nm $\lambda_{emission}$=340 nm	–	0–40 ppb	–	(Soto et al. 1982)
Fe^{3+}-2,3-H_2ND-Bu_3N	Extraction spectrophotometry	510	–	0.5–8.0	Masking agents used	(Patrovsky 1970)
Ti-2,3-H_2ND-Bu_3N	Extraction spectrophotometry	400	–	0.1–2.5	Masking agents used	(Patrovsky 1970)
V^{4+}-2,3-H_2ND-Bu_3N	Extraction spectrophotometry	560	–	0.2–5.0	Masking agents used	(Patrovsky 1970)
Mo-2,3-H_2ND-Bu_3N	Extraction spectrophotometry	390	–	0.3–6.0	Masking agents used	(Patrovsky 1970)
B-2,3-H_2ND-CV	Extraction spectrophotometry	586	1.0×10^5	–	ClO_4^- and SCN^-	(Sato and Uchikawa 1980)
Mo(VI)-2,3-H_2ND-iodonitrotetrazolium chloride	Extraction spectrophotometry	370	9.6×10^3	0.24–17.0	Fe(III), Al(III), Cr(III), Nb(V), Ti(IV), Ge (IV), Mg(II)	(Lekova et al. 2003)
W(VI)-2,3-H_2ND-iodonitrotetrazolium chloride	Extraction spectrophotometry	420	9.38×10^3	0.7–7.4	Fe(III), V(V), Cr(III), Nb(V), Mo(VI)	(Dimitrov and Alexandrov 1995)
Ti-2,3-H_2ND-iodonitrotetrazolium chloride	Extraction spectrophotometry	370	2.57×10^4	0.24–5.2	W(VI), Mo(VI), Cr(III), Fe(III), SCN^- citrate	(Kostova et al. 2000)
V(V)-2,3-H_2ND-iodonitrotetrazolium chloride	Extraction spectrophotometry	340	2.5×10^4	0.1–0.9	UO_2(II), Nb(V), Ti(IV), NO_3^- and SCN^-	(Simeonova et al. 2006)
V(V)-2,3-H_2ND-tetrazolium violet	Extraction spectrophotometry	342	1.5×10^4	0.57–1.7	Cu(II), Al(III), Fe(III), Mo (VI), Re(VII), W(IV), Cr(VI), Nb(V), Ti(IV), NO_3^-	(Lekova et al. 2007)
Mn(II)-2,3-H_2ND-en-H_2O_2	Fluorimetry	$\lambda_{excit.}$=400 nm $\lambda_{emission}$=500 nm	–	10–140 ppb	–	(Watanabe et al. 1995)
$[Fe(H_2ND)_n]$	Voltametry	–	–	–	–	(Obata and Van den Berg 2001)
B-2,3-H_2ND-insulin	Flow injection	–	–	0–0.5 ppm	–	(Iwata et al. 2007)
Ti(IV)-2,3-H_2ND	Aqueous as well as extractive spectrophotometry	390	3.2×10^4	0.02–4.0	Fe(III), Mn(II) and Nb(V)	(Tarafder et al. 1994, Mondal and Tarafder 2004)
Fe^{3+}-2,3-H_2ND	Spectrophotometry	510	1.2×10^4	0–5.0	V(V) and Ti(IV)	(Tarafder and Sardana 2000)
REEs-2,3-H_2ND	Spectrophotometry	655	5.5×10^4	0.01–2.0	Al, Fe and Zr	(Tarafder et al. unpublished data)
UO_2(II)-2,3-H_2ND-CTA^+	Extraction Fluorimetry	$\lambda_{excit.}$=365 nm $\lambda_{emission}$=565 nm	–	0.01–1.0 µg	Mn, Co and Cr	(Tarafder et al. 2002)
Mn-2,3-H_2ND-CTA^+	(i) Extractive spectrophotometry (ii) Extraction AAS (flame as well as GF-AAS)	547	1.2×10^4	0.04–5.0 Flame: 1.0–4.0 GF-AAS: 1.0–10.0 ppb	V(V) and Fe(III)	(Tarafder et al. 2004, Tarafder and Pradhan 2007)
Z_2^{+Na+}[REEs-2,3-H_2ND]	Liquid-liquid extraction	–	–	–	–	(Takayauagi and Yotsuyanagi 1994)
Fe^{3+}-2,3-H_2ND-CTA^+	Extraction spectrophotometry	455	1.2×10^4	0.03–5.0	Mn and UO_2(II)	(Tarafder and Mondal, Unpublished data)

Table 1 (Continued)

Systems	Application in the field	λ_{max} (nm)	ε (l/mol/cm)	Beer's law range (mg/l)	Interference	Reference
Nb(V)-2,3-H_2ND-CH_3COO^-	Extraction spectrophotometry	395	4.6×10^4	0–5.0	Ti(IV), V(V) and Fe(III)	(Tarafder et al. 2009)
Th(IV)-2,3-H_2ND	Spectrophotometry	655	5.0×10^4	0.01–5.0	Zr	(Tarafder et al. Unpublished data)
Mo(VI)-2,3-H_2ND	Spectrophotometry	410	1.0×10^4	0.05–20.0	Ti, Fe, Nb	(Tarafder and Mondal 2007)

2,3-H_2ND, 2,3-dihydroxynaphthalene; Bu_3N, tributylamine; CV, crystal violet; en, ethylenediamine; CTA^+, cetyltrimethylammonium ion; Z_2^+, benzyldimethyltetradecylammonium ion.

over the pH range 8–10 was used for the spectrophotometric determination of iron in aqueous solution. However, the method was made more selective and robust by extracting the reddish-orange anionic complex into ethyl acetate under the influence of cetyltrimethylammonium (CTA) cation, and then measuring the absorbance of the complex in ethyl acetate (Tarafder and Mondal, Unpublished data). The molar absorptivity and Sandell's sensitivity of the complex are 1.2×10^4 l/mol/cm and 0.001 μg/cm^2, respectively. The method has been found very useful in the determination of iron in silicate rocks, ores, sediments, soils and allied products.

Similarly, in our laboratory, a highly sensitive and selective aqueous and extraction spectrophotometric method has been developed for the determination of titanium in silicate (Tarafder et al. 1994) rocks. 2,3-H_2ND forms a yellowish-orange chelate with Ti(IV) which is readily extracted into ethyl acetate over the pH range 4–9. The method is highly sensitive (ε=3.2×10^4 l/mol/cm) and free from interference of most elements present in silicate rock matrices. The method is two-fold more sensitive than tiron, chromotropic acid and diantipyrilmethane methods. Interestingly, unlike the above methods, by selective extraction of the Ti-2,3-H_2ND complex into organic solvents, interference from iron, V, Nb, Mo, Mn, etc. have been eliminated. The application of the method has been further extended to columbite-tantalite minerals for the selective determination (Mondal and Tarafder 2004) of titanium. Niobium present in the minerals seriously interferes in the determination of titanium by most methods including the well-known hydrogen peroxide method. However, titanium in these samples could be accurately determined using the 2,3-H_2ND method by selectively separating Ti(IV) from the niobium rich matrix of columbite-tantalite minerals by solvent extraction carried out at controlled pH.

Recently in our laboratory, an interesting and useful extraction spectrophotometric (Tarafder et al. 2004) method has been developed for the accurate determination of manganese in diverse samples, including rock, minerals, ores, soils, sediments, waters and plant ash. The method developed is unique in the sense that 2,3-H_2ND forms an anionic chelate with manganese, irrespective of its valance states. This is readily extractable into ethyl acetate under the influence of a counter cation, CTA^+, displaying a distinct color (bluish-violet), characteristic of manganese. The reaction is very specific to manganese. Manganese can be determined with a high degree of accuracy (results attested from those obtained from atomic absorption spectrophotometer (AAS) and inductively coupled plasma-atomic emission spectroscope (ICP-AES) at ppm to percentage (%) level after prior removal of iron by resorting to solvent extraction of Fe^{3+} at pH 4–5 using the same reagent (2,3-H_2ND). The application of the method was further extended to the ultra trace determination (Tarafder and Pradhan 2007) of manganese in water samples by pre-concentrating manganese by co-precipitating it along with hydrated iron oxide, dissolving the precipitate in dilute HCl and determining the pre-concentrated manganese using graphite furnace-atomic absorption spectrophotometer (GF-AAS) after extracting the Mn-2,3-H_2ND-CTA ternary complex into ethyl acetate and stripping off of the metal in aqueous solution. A prior separation of iron by solvent extraction at pH 4–5 using the same reagent completely eliminated iron used for co-precipitating manganese. The method is highly selective with molar absorptivity (ε) being 1.2×10^4 l/mol/cm and yields highly reproducible results for manganese determinations.

Very recently, a novel method has been developed for the extraction spectrophotometric determination (Tarafder et al. 2009) of niobium in silicate rocks and columbite-tantalite minerals. The method is based upon the formation of a ternary complex of niobium(V) [Nb(V)] with 2,3-H_2ND and acetate ion in the pH range 8–10. The ternary complex displays a yellowish-orange color on extraction into ethyl acetate. The complex absorbs maximum at 390 nm. The molar absorptivity and Sandell's sensitivity of the method are 4.6×10^4 l/mol/cm and 2 ng/cm^2, respectively. The detection and determination limit of the method are 20 ng/ml and 60 ng/ml, respectively. Because Ti(IV) also absorbs at this wavelength, a prior extraction at pH 4–5 using the same reagent (2,3-H_2ND) completely removes Ti(IV) along with Fe^{3+}, V(V), etc., thereby rendering the method more selective. The method was applied to a host of silicate rocks as well as a set of columbite-tantalite minerals. The results obtained were found to be in excellent agreement with those obtained from the standard thiocyanate method and ICP-AES method.

It is worth mentioning here that the binary complex of Nb(V) with 2,3-H_2ND is not suitable for spectrophotometric measurements because its sensitivity is very low (ε=<10,000 l/mol/cm) and precision of results obtained is also not good. Therefore, the novel ternary system has substantial advantages over the corresponding binary system. In addition to the color complexes formed of 2,3-H_2ND with various metal ions, several colorless complexes, having analytical relevance have been formed of certain elements, such as, UO_2^{2+}, Th, Zr, rare earth elements (REEs), etc.

In our laboratory a useful fluorimetric method (Tarafder et al. 2002) for the determination of uranium has been developed using the reagent 2,3-H_2ND. The reagent, 2,3-H_2ND forms a 1:3 anionic complex with UO_2^{2+} at pH 10–12. The anionic complex is extracted into ethyl acetate using a counter cation, CTA^+, leaving many interfering ions in aqueous solution. However, prior extraction at pH 4–5 using the same reagent has completely removed iron which when present at 10% level in the sample interferes in the fluorimetric determination of uranium by quenching the fluorescent intensity of uranium. Along with iron, many other elements which quench, although to a lesser extent, the uranium fluorescence are also removed through this extraction. These elements include Th, Al, V, Cu, Ni, etc.

The seriously quenching elements such as Mn, Co and Cr are also extracted along with uranium, thereby seriously interfering in the fluorimetric determination of uranium. However, EDTA completely masks these elements, and as such does not allow these three culprit elements to be extracted along with uranium, thereby rendering the method rather selective for the estimation of uranium.

Thorium also forms 1:2 neutral complex with 2,3-H_2ND in the pH range 4–10. This complex is readily extracted into ethyl acetate without any counter cation. However, at pH 4–5 the extraction is never complete, i.e., the extraction is around 80%. Nearly 20% thorium remains in aqueous solution even after using salting-out agent such as saturated sodium acetate. At an elevated pH, i.e., 8–10 >99% thorium is extracted into ethyl acetate in the presence of high concentration of sodium acetate. The extraction behavior of REEs has been observed to be somewhat similar to that of thorium. Unlike thorium, the REEs are not at all extracted into ethyl acetate at pH 4–5 even in the presence of salting-out agents. However, as observed in the case of thorium around >99% REEs are extracted into ethyl acetate at pH 8–10 in the presence of very high concentration of sodium acetate.

Interestingly, a procedure has been evolved (Tarafder et al. Unpublished data) for the separation of thorium from REEs for their selective separation and sensitive spectrophotometric determination using arenazo III after solvent extraction of REEs and Th at pH 8–10 in the presence of high concentration of sodium acetate followed by selective stripping off of REEs at pH 6.2±0.1 into water leaving thorium in the organic phase. After stripping off of Th into water at still lower pH, both REEs (total) and Th could be accurately determined by arsenazo III separately. By making use of the different solvent extraction and stripping behavior of REEs, thorium and uranium, their selective determinations in monazite and related samples is possible.

In our laboratory, based upon the above philosophy, selective hydrometallurgical extraction of uranium, thorium and rare earth from monazite and bastnaesite minerals is in progress. In addition to the above, development of a novel technique for the selective extraction and purification of molybdenum from molybdenum concentrates and its spectrophotometric determination using the reagent 2,3-H_2ND is in progress (Tarafder and Mondal 2007, Tarafder et al. Unpublished data).

Concluding remarks

During the past decade, the reagent 2,3-H_2ND has been widely studied in the field of inorganic chemistry, mostly in the formation and characterization of a host of co-ordination complexes. Apart from this, the readily available compound has been extensively used for the liquid-liquid extraction and spectrophotometric determination of several elements in samples of diverse matrices. A sizable amount of research has been carried out in the authors' laboratory. Owing to its extremely high complex forming ability, this ligand could still prove more useful for its various analytical applications in the future.

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