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Review

Complexes of aminobenzoic acids: A comprehensive review concerning synthesis, physical chemistry, structure and application

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ABSTRACT

The literature studies on the complexes of aminobenzoic acids, especially fenamates, with transition, post-transition and rare earth metals reveal a great interest in this subject. In this paper the binary and ternary complexes of aminobenzoic acids involving oxygen-, nitrogen- and phosphorus-donor coligands were described. We compared the complexes' synthesis methods, their physicochemical properties, spectroscopic studies as well as composition and geometry. The complexes have been characterized in terms of their biological activity and applications as medicals, hybrid organic–inorganic materials, luminescent materials, green corrosion inhibitors, catalysts and magnetic materials.

Abbreviations: 1,2-diMeHim, 1,2-dimethylimidazole; 2,6-pydime, 2,6-dimethanolpyridine; 2,9-Me-phen, 2,9-dimethyl-1,10-phenanthroline; 2-Cl-m-aba, 5-amino-2-chlorobenzoate; 2-Cl-m-Haba, 5-amino-2-chlorobenzoic acid; 2-MeHim, 2-methylimidazole; 2-NH_2-4-Me-py, 2-amino-4-methylpyridine; 2-pyme, 2-pyridinemethanol; 3,4,7,8-Me-phen, 3,4,7,8-tetramethyl-1,10-phenanthroline; 3,5-Cl-anth, 2-amino-3,5-dichlorobenzoate; 3,5-Cl-Hanth, 2-amino-3,5-dichlorobenzoic acid; 3-pyme, 3-pyridinemethanol; 4,7-Me-phen, 4,7-dimethyl-1,10-phenanthroline; 4,7-Ph-phen, 4,7-diphenyl-1,10-phenanthroline; 4-Me-m-aba, 3-amino-4-methylobenzoate; 4-Me-m-Haba, 3-amino-4-methylobenzoic acid; 4-Cl-anth, 2-amino-4-chlorobenzoate; 4-Cl-Hanth, 2-amino-4-chlorobenzoic acid; 4-Cl-m-aba, 3-amino-4-chlorobenzoate; 4-Cl-m-Haba, 3-amino-4-chlorobenzoic acid; 4-MeHim, 4-methylimidazole; 5-Cl-anth, 2-amino-5-chlorobenzoate; 5-Cl-Hanth, 2-amino-5-chlorobenzoic acid; 5-NO_2-anth, 2-amino-5-nitrobenzoate; 5-NO_2-Hanth, 2-amino-5-nitrobenzoic acid; 5-NO_2-phen, 5-nitro-1,10-phenanthroline; ABTS, 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) radical cation; Ar, aryl; bipy, 2,2′-bipyridine; bipyam, 2,2′-bipyridylamine; BSA, bovine serum albumin; Bu, n-butyl; caf, caffeine; CH_2Cl_2, dichloromethane; $CHCl_3$, chloroform; CN, coordination number; cod, cyclo-octa-1,5-diene; CT-DNA, calf thymus DNA; dca, dicyandiamide; dea, diethanolamine; dena, *N*,*N*-diethylnicotinamide; DMF, *N*,*N*-dimethylformamide; dmpa, 2-[(2,6-dimethylphenyl)amino]benzoate; DMSO, dimethyl sulfoxide; DPPH, 2,2-diphenyl-1-picrylhydrazyl; en, ethane-1,2-diamine; Et_2O, diethylether; EtOH, ethanol; flu, flufenamate; H_2biim, 2,2′-biimidazole; Hanth, 2-aminobenzoic acid; Hdmpa, 2-[(2,6-dimethylphenyl)amino]benzoic acid; Hflu, flufenamic acid; Him, imidazole; HL, aminobenzoic acid; Hmeclo, meclofenamic acid; Hmef, mefenamic acid; Hmes, 5-amino-2-hydroxybenzoic acid; Hpas, 4-amino-2-hydroxybenzoic acid; Hpko, 2,2′-dipyridylketone oxime; HSA, human serum albumin; Htolf, tolfenamic acid; K_b, DNA-binding constant; K_{BSA}, BSA-binding constant; K_{HSA}, HSA-binding constant; K_{SV}, Stern–Volmer constant; L, aminobenzoate ligand; L′, coligand; LOX, lipoxygenase; m-, meta; m-aba, 3-aminobenzoate; meclo, meclofenamate; MeCN, acetonitrile; mef, mefenamate; MeOH, methanol; mes, 5-amino-2-hydroxybenzoate; m-Haba, 3-aminobenzoate; ML, binary complexes; MLL′, ternary complexes; M^{n+}, transition and post-transition metal ions; mpc, methyl-3-pyridylcarbamate; N,N-Me-m-aba, 3-(dimethylamino)benzoate; N,N-Me-m-Haba, 3-(dimethylamino)benzoic acid; N,N-Me-p-aba, 4-(dimethylamino)benzoate; N,N-Me-p-Haba, 4-(dimethylamino)benzoic acid; na, nicotinamide; nic, nicotine; NN′en, N^1,N^2-dimethylethane-1,2-diamine; NNen, N^1,N^1-dimethylethane-1,2-diamine; NSAID, non-steroidal anti-inflammatory drug; o-, ortho; OLED, organic light-emitting diode; p-, para; p-aba, 4-aminobenzoate; panth, 2-phenylaminobenzoate; pas, 4-amino-2-hydroxybenzoate; PBu_3, tributylphosphine; Pen, propane-1,3-diamine; Ph, phenyl; p-Haba, 4-aminobenzoic acid; pHanth, 2-phenylaminobenzoic acid; phen, 1,10-phenanthroline; py, pyridine; R, alkyl; RE^{3+}, rare earth metal ions; ROS, reactive oxygen species; SOD, superoxide dismutase; Ten, N^1,N^1, N^2,N^2-tetramethylethane-1,2-diamine; THF, tetrahydrofuran; tolf, tolfenamate; Λ_m, molar conductivity.

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1. Introduction

The aminobenzoic acids are compounds, in which amino and carboxyl groups are directly bounded to aromatic ring. The primary compounds of this group are unsubstituted isomers (o-, m- and p-) of aminobenzoic acid. Anthranilic acid (2-aminobenzoic acid), m-aminobenzoic acid (3-aminobenzoic acid), p-aminobenzoic acid (4-aminobenzoic acid) and their derivatives that contain additional functional groups, aliphatic, aromatic or halogen substituents are extensively used in many areas of industry and chemistry [1–41].

Anthranilic acid derivatives, especially fenamates (mefenamic, flufenamic, meclofenamic, tolfenamic acids), 5-amino-2-hydroxybenzoic acid (mesalazine), 4-amino-2-hydroxybenzoic acid (p-aminosalicylic acid) are compounds with commonly known biological activity. In addition, they belong to non-steroidal anti-inflammatory drugs (NSAIDs), which are used as anti-inflammatory, analgesic and antipyretic agents. Considering industrial application, they are frequently used in production of dyes, pigments and saccharin, UV absorbers, corrosion inhibitors, mold inhibitors in soya sauce, pesticides, explosive funds as well as they may be used as starting materials for the synthesis of compounds with biological, radioprotective or fluorescent properties [1–41].

Moreover, aminobenzoic acids have attracted interest as ligands in metal complexes in recent years which may be noticed by the growth in the number of relevant publications.

Literature survey reveals that researchers' attention is attracted by complexes of aminobenzoic acids with transition, post-transition as well as rare earth metal ions. Considering the number and type of constituent ligands these complexes can be divided into the following two groups.

1. Binary complexes (ML). This group is limited to complexes that, apart from aminobenzoic acid or its anion, do not contain second ligand in their structure.
2. Ternary complexes (MLL′). In this group, the coordination of central ion takes place by donor atoms derived from aminobenzoate ligand (L) as well as coligand (L′).

The purpose of this review is to summarize previous works (that have been published before March 2017) on complexes of twenty aminobenzoic acids in which they play the role of primary ligands.