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Coordination Chemistry of Salicylic Acid

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Abstract: *The complexation of metals with ligands can drastically change the physico–chemical and biological properties of the metal species. The large number of ionizable sites in the ligand molecule, mainly phenolic and carboxylic groups, provide the appreciable ability to form stable complexes and chelates with heavy metal cations (Pb(II), Cu(II), Zn(II) and Cd(II)). In this paper We would like to review the transition metal complexes of salicylic acid.*

Keywords: *Metal complex, microbicidal activity, salicylic acid (SA),*

I. Introduction

1.1 Importance of Salicylic Acid

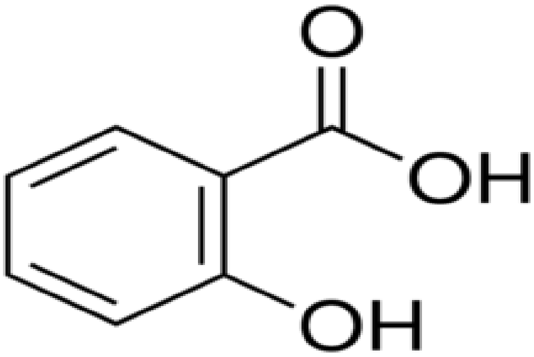

FIG 1. Salicylic Acid

Salicylic acid is of great importance as complexing reagent in analytical chemistry. It is also important in other fields of chemistry, as well as in biology and medicine. Due to the fact that many of the important functions of salicylic acid occur through metal ion complexation. Salicylic acid ($C_7H_6O_3$) is a phenolic phytohormone and is found in plants with roles in plant growth and development[1]. Salicylic acid is biosynthesized from the amino acid phenylalanine and can be produced by sodium salicylate[2,3]. In modern medicine, salicylic acid and its derivatives are used as constituents of some rubefacient products. For example, methyl salicylate is used as a liniment to soothe joint and muscle pain, choline salicylate is used typically to relieve the pain of aphthous ulcers[4]. It is also used as an anti-inflammatory drug[5].

1.2 Coordination Modes

The salts and esters of salicylic acid are known as salicylates. Salicylates are widely used in medicine and have multiple effects on the metabolic processes[6] and also have industrial applications. Transition metal ions form many biologically important complexes with salicylates. In recent reports, metal carboxylates have been extensively studied not only due to their interesting electro-conductive, optical, and magnetic properties[7], From the coordination chemistry point of view, salicylic acid is a versatile ligand for chelating metal ion, since it can offer two hard and strongly basic O-donor centers either from both of carboxylic and hydroxyl group or only from the carboxylic group as a bidentate chelator. The carboxylic group can bind to metal ion in various modes, such as monodentate, bidentate, and bridging[8]. For instance, salicylic acid in a dimeric terbium complex has been found to be coordinated in three ways[9]. In a nanonuclear manganese complex with benzoic and salicylic acids, the anion Sal^{2-} is coordinated in a pentadentate chelating μ 3 -bridging fashion[10]. Due to the maximum bidentate structure of salicylic acid it has the possibility of forming chelates with more than one ligand in the complex species.

II. Related Literature Work

2.1 Transition Metal Complexes

Salicylic acid complexes of Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2} and Cr^{+3}, Mn^{+3}, Fe^{+3}, Co^{+3} metal ions were synthesized in ethanol solution. It was observed that the divalent ions gave better yield than the trivalent ones. The complexes were characterized and inhibition properties of the complexes against three fungi showed that the complexes have higher antimicrobial activity than the ligand which could be attributed to chelation. It appeared that the antifungal activity increased with decrease in ionic size[11]. The inhibitory ability of the metal complexes is notably higher than the ligand and the actions against Aspergillus niger and Aspergillus hereus are comparatively same but greater than that of Trychophyton mantagrophytes. In all, the cobalt complexes showed the highest activity, antimicrobial activity of the metal chelates can be explained on the basis of chelation theory.

The transition metal complexes of Cu^{2+} ,Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} and Fe^{3+} of Benzimidazole-SA have been prepared and characterized by elemental analyses, spectral studies, magnetic moment determination, molar conductivity measurement and microbicidal activity[12]. Some metal ions (Mn^{+2} ,Fe^{+2} ,Co^{+2} ,Cu^{+2} ,Zn^{+2} ,Cd^{+2} and Hg^{+2}) Complexes of salicylic acid (SA) and Pyridine (Py) were Synthesized and characterized by elemental analysis FT-IR and uv-Visible Spectra and conductive measurements[13]. A reaction of iron nitrate with magnesium salicylate and reactions of iron and cobalt chlorides with ammonium salicylate in the presence of water, methanol, DMAA, and DMF gave the trinuclear heterometallic complexes and their X-ray structures were studied[14].

2.1.1 Cu(II)-SA Complex As Catalyst

Cu(II) complexes of salicylic acid are of interest from both structural and biological view points. For example, dinuclear Cu(II) salicylates are biologically interesting owing to their anti-inflammatory activity[15]. other Cu(II) salicylates can show superoxide dismutase activity[16], which may be used in the photodynamic therapy[17]. Because of the importance of the copper complex of salicylic acid, many papers have previously been published about this system[18-24]. The calcium complexes of salicylic acid are reported to be less stable than the corresponding copper complexes[25-28]. Salicylic acid is an efficient and versatile ligand in a variety of Cu (II)-catalyzed cross-coupling reactions. The $CuCl_2$ /salicylic acid mixture catalyzed cross-coupling reactions for aryl alkyne bond formations. A new, efficient, and inexpensive $CuCl_2$ /salicylic acid catalytic system has been developed to catalyze Sonogashira-type cross-coupling of haloarenes and iodoheteroarenes with terminal alkynes under mild reaction conditions to afford the corresponding coupling products in 18-95% yields[29].

2.2 Mono Chelate Salicylatoborates

Salicylic acid is a well known complexing agent with boric acid[30-32]. Several bis-salicylatoborate complexes have been reported in the literature[33-41] of which lithium bis-salicylatoborates have found applications as electrolytes for Li-ion batteries. Salicylatoborate complexes with bioactive cations might therefore be considered as potential micronutrients and pharmacophores aiding in the treatment of metal ion or boron deficiencies and in strengthening the immune system. Lithium mono-salicylatoborate, $Li[B(Sal)(OH)_2]$, was isolated in crystal form and presented as a novel hybrid metal–organic framework possessing zeolitic structure[42].

2.3 Humic Acid Complexes

The stability of metal–humate complexes is an important factor determining and predicting speciation, mobility and bioavailability of heavy metals in the environment. A comparative investigation of the complexation of Cu(II) and Pb(II) with humic acid and humic-like ligands, such as benzoic and salicylic acid, was performed. It was found that Cu(II) and Pb(II) form mononuclear complexes with benzoic and humic acid while with salicylic acid bothmetals form polynuclear complexes. The Cu(II)–salicylate and Pb(II)–salicylate complexes showed noticeable higher stability constants compared with their complexes with humic acid, while the stabilities of the complexes with benzoic acid differed less[43] .

III. Conclusion

This review mainly focus on complexes of salicylic acid with different metals, their spectroscopical studies and biological importance. The salicylic acid is versatile in forming chelates, can act as catalyst. These active metal complexes may serve as a starting point for further studies on metal complexes acting as drugs.

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References

[1]. S. Hayat, A.Ahmad, "Salicylic acid–a plant hormone", London, 2007.

[2]. Diarmiud Jeffreys, "Aspirin the remarkable story of a wonder drug", Bloomsubry, 2005, 38-40.

[3]. A. M. Philip , "Brief History of Antipyretic Therapy Clinical infection Diseases", London, 2000, 154-156.

[4]. H. Wecker and A. Laubert , "Reversible hearing loss in acute salicylate", New York, 52- 65, 2000.

[5]. RK. Madan, J. Levitt, "J Am Acad Dermatol., 70(4), 2014, 788–792

[6]. L. S. Goodman, A. Gilman, The pharmacological basis of therapeutics, New York, 1975.

[7]. (a)J. M. Lehn, Supramolecular Chemistry, Concepts and Perspectives; VCH: Weinheim, 1995; (b) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M.Yaghi, Acc. Chem. Res., , 34, 2001, 319; (c) O. Maury, H. L. Bozec, Acc. Chem. Res. 38, 2005, 691; (d) G. B. Deacon, R. Phillips, J. Coord. Chem. Rev., 33, 1980, 227.

[8]. (a) C. N. R. Rao, ; S. Natarajan, ; R. Vaidhyanathan, Angew. Chem., Int. Ed. 43, 2004, 1466; (b) G. Prabusankar, R. Murugavel, Organometallics., 23, 2004, 5644; (c) R. Murugavel, S. Banerjee, Inorg. Chem. Commun. 6, 2003, 810; (d) R. Murugavel, D. Krishnamurthy, M. Sathiyendiran, J. Chem. Soc., Dalton Trans., 34, 2002; (e) R. Murugavel, K. Baheti, G. Anantharaman, Inorg. Chem. 40, 2001, 6870; (f) R. Murugavel,; V. V. Karambelkar, G. Anantharaman, M. G. Walawalkar, Inorg. Chem. 39, 2001, 1381.

[9]. Ming-Cai Yin, Chang-Chun Ai, Liang-Jie Yuan, et. al., J. Mol. Struct., 33, 2004, 691.

[10]. A.R. Shake, H.L.Tsai, R.J. Webb et al, Inorg. Chem., 33(26), 1994, 6020.

[11]. S. G. Yiase, S. O. Adejo*, J. A. Gbertyo and J. Edeh, IOSR Journal of Applied Chemistry ., 7(4), 2014, 04-10.

[12]. K. V. Patel and A. Singh, E-Journal of Chemistry., 6(1), 2009, 281-288.

[13]. H. A. Sana Journal of Al-Nahrain University., 15 (3), 2012, 23-29.

[14]. V.V. Gorinchoy, V.E. Zubareva, S.G. Shova, V.N. Szafranski, J. Lipkowski, N. Stanica, Yu.A. Simonov, C.I. Turta, Russian Journal of Coordination Chemistry., 35(10), 2009, 731–739

[15]. (a) J. R. J. Sorenson, W. Hangarter, Inflammation., 2, 1977, 217; (b) P. Lemoine, B. Viossat, G. Morgant, F.T. Greenaway, A. Tomas, N.H. Dung, J.R.J. Sorenson, J. Inorg. Biochem., 89, 2002, 18; (c) M.T. Garland, J.Y. Le Marouille, E. Spondine, Acta Crystallogr., Sect. C., 41, 1985, 855.

[16]. (a) C. L. O' Young, S. J. Lippard, J. Am. Chem. Soc. 102, 1980, 4920; (b) J. R. J. Sorenson, J. Med. Chem., 27, 1984, 1747.

[17]. M. Athar, C. A. Elmets, M. T. Zaim, J. R. Jenifer, D. R. Bickers, H. Mukhtar, Proc. SPI Int. Soc. Opt. Eng., 847, 1988, 193.

[18]. A.K. Babko, Zh. Obshch. Khim., 17, 1947, 443.

[19]. A.M. Vasiliev and V.M. Gorokhovski, Uch. Zap. Kaz., 8, 1953, 65.

[20]. D.D. Perrin, Nature, 182, 1958, 741.

[21]. C. Heitner-Wirguin and R. Cohen, Bull. Soc. Chim. Ft., 27, 1960, 293.

[22]. Y. Hsiu-Chin, Acta Chim. Sinica., 32, 1966, 94.

[23]. G.M. Habashy, J. Electroanal. Chem., 21, 1969, 357.

[24]. V.K. Zolotukhin, Visn. L'viv. Univ., Ser. Khim., 12, 1971, 44.

[25]. C.W. Davies, J. Chem. Soc., 1938, 277.

[26]. N.R. Joseph, J. Biol. Chem., 164, 1946, 529.

[27]. R.P. Bell and G.M. Waind, J. Chem. Soc., 1951**,** 2357.

[28]. J. Schubert, J. Amer. Chem. Soc., 76, 1954, 3442.

[29]. Horung-Jyh Chen, Zhe-Yi Lin, Meng-Yuan Li, Ruei-Jheng Lian, Qing-Wen Xue, Jui-Lun Chung, Shu-Chih Chen, Yao-Jung Chen, Tetrahedron., 66. 2010, 7755-7761.

[30]. J. Böeseken, J. Meulenhoff, Proc. Acad. Sci. 27, 1924, 174.

[31]. J. Böeseken, A. Niks, Rec. Trav. Chim. Pays-Bas., 59, 1940, 1062.

[32]. A. Queen, Can. J. Chem., 55, 1977, 3035.

[33]. P. Li, Z.-H. Liu, Z. Kristallogr. NCS., 221, 2006, 179.

[34]. J. Zhang, J. Wang, X.-Y. Huang, J.-T. Chen, Z. Kristallogr. NCS 220, 2005, 261.

[35]. A. Downard, M. Nieuwenhuyzen, K.R. Seddon, J.-A. van den Berg, Cryst. Growth Des., 2, 2002, 111.

[36]. I.I. Zviedre, E.M. Shvart, V.K. Belskii, Zh. Neorg. Khim., 44, 1999, 1994.

[37]. V. Cody, Acta Cryst. C40., 1984, 1214.

[38]. J. Bassett, P.J.J. Matthews, Inorg. Nucl. Chem. 40, 1978, 987.

[39]. Z.-M. Xue, K.-N. Wu, B. Liu, C.-H. Chen, J. Power Sources., 171, 2007, 944.

[40]. Y. Sasaki, M. Handa, K. Kurashima, T. Tonuma, K. Usami, J. Electrochem. Soc. 148, 2001, A999.

[41]. J. Barthel, R. Buestrich, H.J. Gores, M. Schmidt, M. Wühr, J. Electrochem. Soc. 144, 1997, 3866.

[42]. Dursun Ali Köse , Birgül Zümreoglu-Karan , Tuncer Hökelek, Ertan Sahin, Inorganica Chimica Acta., 363, 2010, 4031–4037

[43]. Ivana kostic, Tatjana andelkovic, Ruzica nikolic, Aleksandar bojic, Milovan purenovic, Srdan blagogevic, Darko andelkovic, J. Serb. Chem. Soc., 76 (9), 2011, 1325–1336.