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SPECTROPHOTOMETRIC DETERMINATION OF Co(II) COMPLEXES WITH N-P- BROMOPHENYLTHIOBENZOHYDROXAMIC ACID

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ABSTRACT: A new Spectrophotometric method has been established for the determination of cobalt (II) ion in formulations. The method based on formation of stable red complex with with n-p- bromophenylthiobenzohydroxamic acid, using spectrophotometric and phosphorimetric methods based on the oxidation of various organic dyes with bromate, iodate and hydrogen peroxide in the presence or absence of activators. However, among the several analytical techniques for the determination of vanadium, spectrophotometric methods are quite popular due to their simplicity and low-cost instrumentation. Inorganic chemistry research in the medical field has been widely developed through the synthesis of new compounds that are thought to have antibacterial activity [1]. Complex compounds consist of metal ions metals that have d orbitals that have not been fully filled by electrons with ligands that have donor atoms. Many new complex compounds that are successfully synthesized provide better results than their free ligands [2]. Complexes with cobalt metal have better antibacterial activity compared to complexes with copper and nickel metals [3]. Some cobalt complexes are also known to have higher antibacterial activity compared to other transition metals [4].

KEYWORDS: spectrophotometric, bromophenylthiobenzohydroxamic, cobalt, complex, ligands, metal complexes, transition

I.INTRODUCTION

In coordination chemistry, a stability constant (also called formation constant or binding constant) is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host-guest complexes and complexes of anions. The stability constant(s) provide(s) the information required to calculate the concentration(s) of the complex(es) in solution. There are many areas of application in chemistry, biology and medicine. There are three major theories relating to the strength of Lewis acids and bases and the interactions between them.[1,2]

1. Hard and soft acid-base theory (HSAB).^[10] This is used mainly for qualitative purposes.
2. Drago and Wayland proposed a two-parameter equation which predicts the standard enthalpy of formation of a very large number of adducts quite accurately. $-\Delta H^\ominus (A - B) = E_A E_B + C_A C_B$. Values of the E and C parameters are available.^[11]
3. Guttmann donor numbers: for bases the number is derived from the enthalpy of reaction of the base with antimony pentachloride in 1,2-Dichloroethane as solvent. For acids, an acceptor number is derived from the enthalpy of reaction of the acid [3,4]with triphenylphosphine oxide.^[12]

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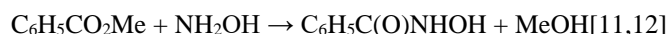
The thermodynamics of metal ion complex formation provides much significant information.^[13] In particular it is useful in distinguishing between enthalpic and entropic effects. Enthalpic effects depend on bond strengths and entropic effects have to do with changes in the order/disorder of the solution as a whole. [5,6]The chelate effect, below, is best explained in terms of thermodynamics. To avoid the complications involved in using activities, stability constants are determined, where possible, in a medium consisting of a solution of a background electrolyte at high ionic strength, that is, under conditions in which Γ can be assumed to be always constant.^[15] For example, the medium might be a solution of 0.1 mol dm^{-3} sodium nitrate or 3 mol dm^{-3} sodium perchlorate. When Γ is constant it may be ignored and the general expression in theory, above, is obtained.[7,8]

All published stability constant values refer to the specific ionic medium used in their determination and different values are obtained with different conditions, as illustrated for the complex CuL ($L = \text{glycinate}$). Furthermore, stability constant values depend on the specific electrolyte used as the value of Γ is different for different electrolytes, even at the same ionic strength. There does not need to be any chemical interaction between the species in equilibrium and the background electrolyte, but such interactions might occur in particular cases. For example, phosphates form weak complexes with alkali metals, so, when determining stability constants involving phosphates, such as ATP, the background electrolyte used will be, for example, a tetralkylammonium salt. Another example involves iron(III) which forms weak complexes with halide and other anions, but not with perchlorate ions.[9,10]

When published constants refer to an ionic strength other than the one required for a particular application, they may be adjusted by means of specific ion theory (SIT) and other theories.^[17]

II.DISCUSSION

In organic chemistry, hydroxamic acids are a class of organic compounds bearing the functional group $\text{R}-\text{C}(=\text{O})-\text{N}(\text{OH})-\text{R}'$, with R and R' as organic residues. They are amides ($\text{R}-\text{C}(=\text{O})-\text{NH}-\text{R}'$) wherein the nitrogen center has a hydroxyl ($-\text{OH}$) substituent. They are often used as metal chelators.^[1] Hydroxamic acids are usually prepared from either esters or acid chlorides by a reaction with hydroxylamine salts. For the synthesis of benzohydroxamic acid, the overall equation is:^[2]



Hydroxamic acids can also be synthesized from aldehydes and N-sulfonylhydroxylamine via the Angeli-Rimini reaction.^[3]

A well-known reaction of hydroxamic acid esters is the Lossen rearrangement.^[4]

The conjugate base of hydroxamic acids forms is called a hydroxamate. Deprotonation occurs at the NOH group. The resulting conjugate base presents the metal with an anionic, conjugated O,O chelating ligand. Many hydroxamic acids and many iron hydroxamates have been isolated from natural sources.^[6]

They function as ligands, usually for iron.^[7] Nature has evolved families of hydroxamic acids to function as iron-binding compounds (siderophores) in bacteria. They extract iron(III) from otherwise insoluble sources (rust, minerals, etc.). The resulting complexes are transported into the cell, where the iron is extracted and utilized metabolically.^[8]

Ligands derived from hydroxamic acid and thiohydroxamic acid also form strong complexes with lead(II).^[9]

Hydroxamic acids are used extensively in flotation of rare earth minerals during the concentration and extraction of ores to be subjected to further processing.^{[10][11]}

Some hydroxamic acids (e.g. vorinostat, belinostat, panobinostat, and trichostatin A) are HDAC inhibitors with anti-cancer properties. Fosmidomycin is a natural hydroxamic acid inhibitor of 1-deoxy-D-xylulose-5-phosphate

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reductoisomerase (DXP reductoisomerase). Hydroxamic acids have also been investigated for reprocessing of irradiated fuel.[13,14]

III.RESULTS

Cobalt compounds are chemical compounds formed by cobalt with other elements. In the compound, the most stable oxidation state of cobalt is the +2 oxidation state, and in the presence of specific ligands, there are also stable compounds with +3 valence. In addition, there are cobalt compounds in high oxidation states +4, +5 and low oxidation states -1, 0, +1. Four halides of cobalt(II) are known, which are cobalt(II) fluoride (CoF₂) which is a pink solid, cobalt(II) chloride (CoCl₂) which is a blue solid, cobalt(II) bromide (CoBr₂) which is a green solid, and cobalt(II) iodide (CoI₂) which is a blue-black solid. In addition to the anhydrous forms, these cobalt halides also have hydrates. Anhydrous cobalt(II) chloride is blue, while the hexahydrate is red-purple.^[1] Because the color change of cobalt(II) chloride in different hydrates, it can be used to manufacture color-changing silica gel.[15,16]

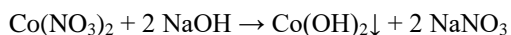
Anhydrous cobalt halides react with nitric oxide at 70~120 °C to generate [Co(NO)₂X]₂ (X = Cl, Br or I). The complex of cobalt halides and triethylphosphine ((C₂H₅)₃P) can absorb nitric monoxide in benzene to form the diamagnetic material Co(NO)X₂(P(C₂H₅)₃)^[2]

In the reaction $\text{Co}^{3+} + \text{e}^{-} \rightarrow \text{Co}^{2+}$

, the potential is +1.92 V, which is higher than that of Cl₂ to Cl⁻ (+1.36 V). Therefore, the interaction of Co³⁺ with Cl⁻ produces Co²⁺ and releases chlorine gas. The potential from F₂ to F⁻ is as high as +2.87 V, and cobalt(III) fluoride (CoF₃) can exist stably. It is a fluorinated reagent and reacts violently with water.^[3]

Cobalt can form various oxides, such as CoO, Co₂O₃ and Co₃O₄. Co₃O₄, at 950 °C, decomposes to CoO.^[4]

Soluble cobalt salts react with sodium hydroxide to obtain cobalt(II) hydroxide (Co(OH)₂):^[5]



Cobalt(II) hydroxide can be oxidized to the Co(III) compound CoO(OH) under alkaline conditions.[17]

Cobalt powder reacts with ammonia to form two kinds of nitrides, Co₂N and Co₃N. Cobalt reacts with phosphorus or arsenic to form Co₂P, CoP, CoAs₂ and other substances.^[2] Cobalt(II) azide (Co(N₃)₂) is another binary compound of cobalt and nitrogen that can explode when heated. Cobalt(II) and azide can form Co(N₃)₂⁻⁴ complexes.^[6] Cobalt pentazolid Co(N₅)₂ was discovered in 2017, and it exists in the form of the hydrate [Co(H₂O)₄(N₅)₂]·4H₂O. It decomposes at 50~145 °C to form cobalt(II) azide, becoming anhydrous and releasing nitrogen, and exploding when heated further. This compound can be obtained by reacting (N₅)₆(H₃O)₃(NH₄)₄Cl^[7] or Na(H₂O)(N₅)·2H₂O^[8] and [Co(H₂O)₆](NO₃)₂ at room temperature. Hydrogen bonding of water stabilizes this molecule.^[8]

Cobalt can easily react with nitric acid to form cobalt(II) nitrate Co(NO₃)₂. Cobalt(II) nitrate exists in the anhydrous form and the hydrate form, of which the hexahydrate is the most common. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) is a red deliquescence crystal that is easily soluble in water,^[9] and its molecule contains cobalt(II) hydrated ions ([Co(H₂O)₆]²⁺) and free nitrate ions.^[10] It can be obtained by precipitation from solution.[18]

IV.CONCLUSIONS

A bromophenol is any organobromide of phenol that contains one or more covalently bonded bromine atoms. There are five basic types of bromophenols (mono- to pentabromophenol) and 19 different bromophenols in total when positional isomerism is taken into account. Bromophenols are produced by electrophilic halogenation of phenol with bromine. There is a total of 19 bromophenols, corresponding to the different ways in which bromine atoms can be attached to the

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five carbon atoms in the benzene ring of the phenol molecule, excluding the carbon atom to which the hydroxy group is attached.

Monobromophenols have three isomers because there is only one bromine atom that can occupy one of three ring positions on the phenol molecule; 2-bromophenol, for example, is the isomer that has a bromine atom in the ortho position. Pentabromophenol, by contrast, has only one isomer because all five available ring positions on the phenol are fully brominated.[19]

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