Simultaneous Preparation of Facial and Meridional Isomer of Cobalt-Amino acid Complexes and their Characterization

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Abstract

Preparation and characterization of various complexes of cobalt (III)-amino acid system, especially cobalt (III) glycinato and cobalt (III) alaninato complexes are reported. The identification of the various isomers of these complexes is also reported. The various isomers are separated from their mixture by fractional crystallization. Each of these complexes has been characterized by observing physical characteristics, chemical analysis, UV-visible spectroscopy and IR-spectroscopy. The direct impact of geometry of the complexes to IR stretching frequencies and UV-visible spectral data of amino and carboxyl group in the complexes provided sufficient information about the geometry. A prediction about the geometries of the synthesized has also been focused.

1. Introduction

The bonding nature of the α-amino acid complexes of Co(III) ion and their spectroscopic investigation have been the subject of much interest since long time perhaps because of their biochemical importance. A knowledge of the interaction between biologically active molecules and metals is needed when preparing biomaterials or considering certain aspects of biocompatibility. The study of model species such as the simple amino acids can assist in the interpretation of more complex system. Amino acid (glycine and alanine) has the neutral donor N at one end and acidic replaceable H at the other end and are sufficient length to span two adjacent coordinating site and the resulting complexes is a non electrolyte chelate or inner complex compound. Such metal chelates are characterized by great thermal stability [7, 11], are intensely colored, insoluble in water but soluble in

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organic solvents are of practical importance. Cis- and trans-bis-(glycino)-platinum(II), $Pt(NH_2CH_2CO_2)_2$, were prepared by Pinkard and co-workers [2] and were twice recrystallized from water. Bis-(glycino)-copper (II) monohydrate, $(Cu(C_2H_4NO_2)_2 \cdot H_2O)$ was prepared by Abderhalden and Schnitzler [2]. There are three complexes of cysteine with cobalt (III) ion were isolated in the solid state by Segbert such as Bis-cysteine of cobalt (III). Shubert concluded that the sulfhydral and carboxyl groups of cysteine were co-ordinated to the cobalt atom. The ultimate goal is to simultaneous synthesis of facial and meridional isomer of some cobalt-amino acid complexes and their characterization. Two isomers of Co(III)-glycine complex are exist; a violet and a red. Both of these two isomers were prepared by the method of Shibata *et al.* [7, 8] here allowing glycine to reacts with aqueous potassium tri(carbonato)cobalt (III). In both isomer coordination is occur via amino ($-NH_2$) and carboxyl group of glycine.

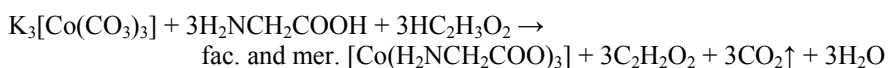## 2. Experimental

2.1. *Chemicals and reagents*

Analytical grade potassium hydrogencarbonate (BDH), cobalt(II) chloride (Merk), 30% hydrogen peroxide (BDH), glycine and alanine, 6N acetic acid are purchased and used without further purification.

2.2. *Instruments*

The UV-visible spectra recorded on an UV-visible spectrophotometer of SHIMADZU, UV-160A model. The infrared spectra were recorded on a Dr-8001, SHIMADZU FT-IR model.

2.3. *Preparation of tris (glycinato) cobalt (III) complex*

Potassium hydrogencarbonate (0.300mol) mixture in 30 ml water is cooled in an ice bath for 15 mins with mechanical stirring. Adding 0.042 mol of cobalt (II) chloride 6-hydrate solution prepared at 30^0C in water. The mixture is allowed to stand for 15 mins in an ice bath, and 15 ml of 30% hydrogen peroxide is then added at a rate of one drop every 5 second, with mechanical stirring at $0-5^0C$, followed by suction filtration. 0.120 mol of glycine is added to the resulting green filtrate of potassium tri(carbonato)cobalt(III).The mixture is heated at $60-70^0C$ until the color of the resulting solution is changes from green to dark blue to violet. Then 6N acetic acid is added slowly at a rate of 1 drop every 5 seconds with mechanical stirring. The solution is stirred vigorously until the evolution of carbon dioxide ceases and the color of the solution has becomes reddish violet.

$$10 \, KHCO_3 + 2 \, CoCl_2.6H_2O + H_2O_2 \rightarrow 2K_3[Co(CO_3)_3] + 4CO_2 \uparrow + 4KCl + 18H_2O$$

$$K_3[Co(CO_3)_3] + 3H_2NCH_2COOH + 3HC_2H_3O_2 \rightarrow$$
$$\text{fac. and mer. } [Co(H_2NCH_2COO)_3] + 3C_2H_2O_2 + 3CO_2\uparrow + 3H_2O$$

The deposited reddish pink crystals of the soluble facial isomer are collected by suction filtration. The filtrate is concentrated in a rotary evaporator until violet crystals of the more soluble meridional isomer are deposited. The molecular structures of both isomers are presented in Figs. 1 and 2.
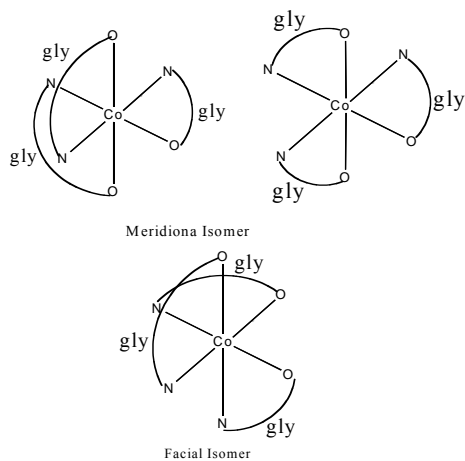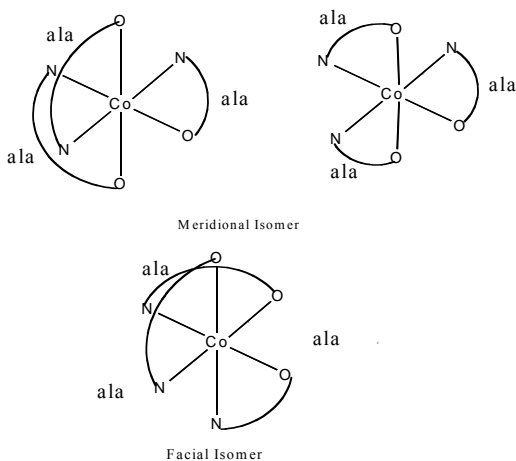
Fig. 1. Meridional and facial isomer of Co(gly)$_3$ complex.

Fig. 2. Meridional and facial isomer of Co(ala)$_3$ complex.

The yields of facial and meridional isomers are 2.1g (18.7%) and 2.7g (24.0%) respectively. If, before addition of the acetic acid, the reaction mixture is heated for an hour after it has become violet, the facial isomer is favored: facial 3.3g (29.3%); meridinal 1.5g (13.3%). On the other hand, if it is heated only until it has become dark blue (about 15 mins), the meridional isomer is favored: facial 0.9g (8.0) and meridional 4.2g (37.4%) [4].

2.4. *Preparation of tris (Alaninato) cobalt (III) complex*

The above procedure can be modified to prepare the corresponding complexes of other amino acids. For examples, if 11.0g alanine is substituted for the glycine and if, before the addition of acetic acid, the reaction mixture is heated for an hour after it has become violet, the yields of the facial and meridional isomer of $[Co(H_2NCH_2CH_2COO)_3]$ are 1.5g (11.6%) and 3.7g (28.6%), respectively.

3. Results and Discussion

3.1. *Physical appearances*

According to Ley and Winkler [4], mer(α)-tris(glycinato)cobalt(III) forms large, dark violet, rhombic crystal contain two molecules of water of crystallization, while fac(β)-Tris (Glycinato)Cobalt(III) formed a reddish pink needle like crystal with one molecule of water of crystallization. In contrast to these results, the pink and violet forms are in anhydrous and monohydrate forms, respectively. The number of molecules of water of crystallization varies with condition of drying. The isomers are not directly convertible. These are soluble only with difficulty in water and in basic solvents such as pyridine and aniline. Both are considerably more soluble in acid solution from which they can be precipitated unchanged by addition of ethanol. As further evidence of their extraordinary stabilities, they can be recovered unchanged from hot concentrated sulfuric acid and can be treated with hot concentrated nitric acid for sometime without noticeable decomposition. Both are decomposed, however, by prolonged warming with concentrated hydrochloric acid, resulting in evolution of chlorine and formation of cobalt(II) chloride [4]. They are virtually insoluble in most organic solvents. The electrical conductance of aqueous and sulfuric acid solutions of both isomers shows these to be non-electrolytes. The two isomers do not react with ammonia at low temperature. But they react with potassium cyanide giving potassium hexacyanocobaltate (III) and potassium glycinate. The red isomer reacts readily with potassium nitrate to give a solution yielding ruby red crystals, whereas the violet isomer under goes this reaction only with difficulty.

3.2. *IR spectra*

Some important IR bands of glycine and alanine are given in Table 1. The location or bonding of the ligands is with the central metal ion, which is manifested mainly by two IR bands like $-COO^-$ and NH_3^+ groups. The rest of the bands are supported by the FT-IR investigation, which is presented in Table 1.

Table 1. Some important IR bands of glycine and alanine in cm^{-1}.

Ligands	NH_3(N-H stretching)	-CH (stretching)	NH_3(N-H) bending	$-COO^-$(asym. stretching.)	$-COO^-$(sym. stretching.)
Glycine	3107 s	2972 w	1498.9 s	1597.3 s	1394.7 s
Alanine	3084.6 m	2865 m	1456.4 s	1586 m	1412.1 s

Some important IR bands of various Co-amino acid complexes are shown in Table 2. The peaks in the 3000 cm^{-1} region for the Co-Amino acid complexes reveal that the N-H stretching vibration is considerably changed on the formation of the nitrogen to metal bond.

It is evident from the IR bands of Co-glycine system that both the symmetric and asymmetric stretching frequencies of NH_3^+(N-H) is increased. The N-H stretching frequency in glycine was assigned as 3107 cm^{-1}. This is increased to 3447.2 and 3229.2 cm^{-1} in facial isomer of [Co(gly)$_3$] and 3447.2 and 3136.6 cm^{-1} in meridional isomer. In Co-alanine system the asymmetric stretching is increased considerably than that of alanine due to creation of inductive effect on nitrogen atom and hence the stability of N-H bond also bond strength is increased. Therefore, the stretching frequency is increased [2].

Table 2. Some important IR bands of various Co-amino acid complexes in cm^{-1}.

| Complexes	NH$_2$ asy. stretching	NH$_2$ sym. stretching	-COO$^-$ (asym. stretching.)	-COO$^-$ (sym. stretching.)	Difference between -COO$^-$(Δf)	M-N Stretching
Fac[Co(gly)$_3$]	3447.2 s	3229.2 s	1684.1 m 1635.8 s	1394.7 m 1373.5 s	298.4 262.3	609.6 m
Mer[Co(gly)$_3$]	3447.2 s	3136.6 m	1684.1 s	1394.7 m 1373.5 s	289.4 310.6	607.7 m
Fac[Co(ala)$_3$]	3219.6 m	2729.6 m 2606.1 m	1660.0 m	1387.0 s 1361.9 s	273.0 298.1	652.0 m
Mer[Co(ala)$_3$]	3096.1 m	2604.1 m	1640.0 m	1412.1 s 1361.9 s	227.9 278.1	650.1 m

s=strong, m=medium, and w=weak.

In all Co-Amino acid complexes the asymmetric (–COO$^-$) stretching frequencies are increased and symmetric (–COO$^-$) stretching frequencies are decreased. The explanation of this observation is that when the –COO$^-$ bonded to metal ions lose or break down of symmetry of octahedral geometry occur.
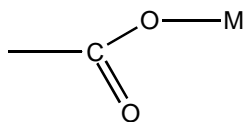
This is consistent with findings in the present study (Table 2) and the mode of chelation of the metal by the ligand may be suggested as [5, 10].
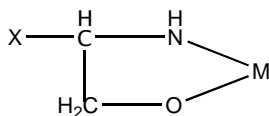
3.3. *UV-visible spectra*

The UV-visible spectrum of starting material and ($CoCl_2.6H_2O$) and complexes are given in Table 3. The following table indicates the concentration, absorption and molar extinction coefficient of various complexes of cobalt-amino acid system.

The two absorption bands of same absorbance obtained at the wavelength of 375 nm and 520 nm. Now, $A = \varepsilon cl$, where, A = absorbance (0.088), c = 7.2×10^{-3} moles/L, l= length of cell (1 cm) and ε is molar absorptivity. The value of ε_{max} was found 12.222 L moles cm^{-1}. Similarly the values of ε_{max} of meridional [Co(gly)$_3$], facial [Co(ala)$_3$], and meridional [Co(ala)$_3$] are obtained 24.805, 68.871, 84.375 L moles cm^{-1}, respectively.

Table 3. UV-visible spectral data for cobalt (III)-amino acid complexes.

Complexes/ligands	Concentration (M) $\times 10^{+3}$	Absorption max. (nm)	Molar extinction coefficient, ε_{max}
$CoCl_2.6H_2O$	8.9	513	7.079
Fac.[Co(gly)$_3$]	7.2	375 & 520	12.222 (375)
Mer.[Co(gly)$_3$]	7.7	376 & 525	24.805 (376)
Fac.[Co(ala)$_3$]	6.2	373 & 544	68.871 (373)
Mer.[Co(ala)$_3$]	6.4	371 & 542	84.375 (371)
Glycine	-----	217	----
Alanine	-----	210	----

The electronic absorption for prepared complexes is collected in Table 3. This result is consistent with the literature value [3, 4]. By comparing the λ_{max} and ε_{max} of these prepared complexes and starting material, it is concluded that they are not same species. For all Co-amino acid complexes the value of ε_{max} are greater than that of $CoCl_2.6H_2O$. It was observed that ε_{max} value of meridional isomer is larger than that of facial isomers of all the complexes. This can be explained on the basis of symmetry. A simple general rule that complex contains symmetrical structure has pale color since splitting is restricted i.e. transition becomes less important and relatively less intense bands were observed. Visual distinction also supports this result. Facial isomer is reddish pink and the meridional isomer is violet. The transitions occurring in Co-amino acid complex are two types. One confined to the d-orbital of the Co atom (ligand field band), other is incipient charge transfer (LMCT or MLCT) [1]. The π orbitals of each carboxylate group would overlap with only one of the three $t_{2g}d$-orbitals of the metal that is the π-orbitals of carboxylate group on the y–axis would overlap the d_{xy}-orbital of the Co^{3+} ion [9]. From these observations, it is concluded that when $-COO^-$ bonded to Co^{3+} ion, the loss or break of symmetry of octahedral geometry takes place [6]. These are consistent with reported work [5].

3.4. *Elemental analysis*

The EDTA titration of various complexes shows the following percentage of Co in those corresponding complexes.

Table 4. Percentage of Co in various complexes.

Complexes	Experimental	Calculated
$CoCl_2.6H_2O$	24.42	24.76
Fac.$[Co(gly)_3]$	20.76	20.76
Mer.$[Co(gly)_3]$	20.46	20.76
Fac.$[Co(ala)_3]$	18.86	18.08
Mer.$[Co(ala)_3]$	18.75	18.08

The entire experimental %Co and the calculated %Co are consistent with the reported one [4]. Other proportion of complex would be ligand. This result supported that one cobalt metal ion bonded to three ligands in Co-amino acid complex system.

4. Conclusions

Various isomers of glycine and alanine complexes of cobalt (III) are prepared in aqueous medium. Because of their solubility difference two isomers are separately crystallized from the solution. In both glycine and alanine cobalt (III) complexes, two types of geometrical isomer of different color is obtained. In *facial isomer* isomers, all of the amino groups of the amino acid molecules are adjacent, while in *meridional isomer*, two of these occupy opposite positions. By comparing the values of ε_{max} in ultraviolet absorption spectra, it was concluded that the larger value is for meridional isomer. We observed the shifting of –COO⁻ and –NH_2 stretching frequencies in the complexes compared to their corresponding ligands which indicate the coordination of ligands to metal ion. In the case of meridional and facial-tris-(glycino)-cobalt (III) isomers the infrared spectra reveal that the reddish pink isomers has the cis (1,2,3)–configuration and the violet meridional isomers has the (1,2,6)–structure. Although neither isomer possesses a center of symmetry, the greater number of bands observed for the compounds suggested that the configuration of the isomer has lower overall order of symmetry as would be expected for a (1,2,3)- structure.

Acknowledgments

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