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Cobalt(II), Copper(II), Zinc(II)—Amino and Thiosalicylic Acids Ternary Complexes

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A series of Co(II), Cu(II), Zn(II)-thiosalicylic-amino acids of the molecular formula (*M-TSA-a.a.*) $\cdot$ 2 H_2O has been synthesized and characterized by chemical analyses, molar conductance, electronic and i.r. spectral measurements.

(Keywords: Complexes, ternary; Molar conductance)

Ternäre Komplexe von Kobalt(II), Kupfer(II) und Zink(II)—Amino- und Thiosalizylsäuren

Es wurde eine Reihe von Co(II), Cu(II) und Zn(II)-Thiosalizyl-Aminosäure Komplexe der allgemeinen Formel (*M-TSA-a.a.*) $\cdot$ 2 H_2O dargestellt und mittels chemischer Analyse, molarer Leitfähigkeit und Elektronen- bzw. IR-Spektren charakterisiert.

Introduction

Generally ternary transition metal complexes containing an amino acid as a one ligand are of significant importance from the biological point of view. A literature survey reveals that little attention has been paid to ternary complexes containing amino acids. Complexes involving 1,10-phenanthroline and α-amino acids have been studied [1]. On the other hand, *Kwik* and *Ang* [2] prepared some Cu(II) complexes of bipyridyl and phenanthroline (N,N donor ligands) and some amino acids. In the present work, we report the isolation of ternary complexes of some divalent transition metal ions, *viz.* Co(II), Cu(II), Zn(II), containing thiosalicylic acid (S, O ligand) as well as one of the following amino acids: glycine (gly), *L*-alanine (ala) and *L*-valine (val). The structure of these complexes were characterized by chemical analysis, electronic and infrared spectra as well as molar conductance measurements.

Experimental

All materials were of Analar® Grade. Stock solutions 0.01 mol metal salts $CuCl_2 \cdot 2\,H_2O$, $CoCl_2 \cdot 2\,H_2O$, $Zn(NO_3)_2 \cdot 6\,H_2O$ and thiosalicyclic acid were prepared by dissolving accurately weighed amounts in the appropriate volume of absolute ethanol. A stock solution of each amino acid was prepared in water-ethanol mixture (1 : 1). Solutions of lower molarity were prepared by accurate dilutions.

The ternary complexes were prepared by slowly addition of 1 mmol of aqueous metal salt solution to 1 mmol solution of amino acid. The mixture was refluxed for 1 h and concentrated. To this solution thiosalicylic ethanolic solution (1 mmol) was added [the reaction mixture turns black in color in the case of Cu(II) and Co(II)] and refluxed for 2 h. The solution was heated till the volume was reduced by approximately half, then cooled, whereby a crystalline product formed. This was filtered off, washed several times with small portions of ethanol and then dried *in vacuo*. In the case of Zn(II), a white precipitate formed on the addition of thiosalicylic acid solution. Microanalysis data and colors of the complexes are reported in Table 1.

The electronic conductance measurements were performed at 25 °C in *DMF* using a Pye conductance bridge. The UV and visible spectra were carried out using matched 1 cm silica cells on a Pye Unicam SP 8-100 spectrophotometer. The i.r. spectra of the complexes were recorded in potassium bromide using a Perkin-Elmer 599 B infrared spectrophotometer.

Results and Discussion

The ternary complexes isolated in the present study are given in Table 1, along with the values of their molar conductance in *DMF*. Generally, the ternary complexes isolated have the general formula $[(M\ (TSA)\ (a.a.)] \cdot (H_2O)_2 \cdot M = Co^{2+}, Cu^{2+}, Zn^{2+}$ and $a.a$ = glycine, alanine, valine. The Cu(II) ternary complexes display a molar conductance $\leqslant 8.1\ \mathrm{Ohm}^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$ indicating the nonelectrolyte nature of such complexes. This suggests that monovalent anions of both thiosalicylic and amino acid moieties are coordinated to the central metal ion. This result is consistent with the formulation suggested by the micro-analysis results (Table 1).

Infrared Spectra

The presence of both two ligands amino and thiosalicylic acids in coordination to the central metal ion is revealed by careful examination of the infrared spectra of the ternary complexes prepared. The significant infrared bands of the different Co(II), Cu(II) and Zn(II) ternary complexes synthesized in this investigation along with their assignment are recorded in Table 2. Generally the recorded infrared spectra of the ternary complexes display a broad band at 3 450–3 400 cm^{-1} suggesting the presence of water molecules in these complexes. This behaviour is substantiated by the results of chemical analyses of the ternary complexes

Table 1. *Chemical analysis, color and molar conductance values of the ternary complexes*

Complex	Colour	Molar Conductance $Ohm^{-1}\ cm^2\ mol^{-1}$	Calculated %		Found %	
			C	S	C	S
$Co(C_7SO_2H_5)\ (C_2H_4O_2N)\ (H_2O)_2$	black	*	33.55	9.95	34.63	10.09
$Co(C_7SO_2H_5)\ (C_3H_6O_2N)\ (H_2O)_2$	olive green	*	35.74	9.54	36.12	10.12
$Co(C_7SO_2H_5)\ (C_5H_{10}O_2N)\ (H_2O)_2$	olive green	*	39.57	8.8	39.92	8.92
$Cu(C_7SO_2H_5)\ (C_2H_4O_2N)\ (H_2O)_2$	black	8.6[a]	33.09	9.81	33.78	9.42
$Cu(C_7SO_2H_5)\ (C_3H_6O_2N)\ (H_2O)_2$	pale green	8.1[a]	35.27	9.41	35.64	9.61
$Cu(C_7SO_2H_5)\ (C_5H_{10}O_2N)\ (H_2O_2)_2$	black	4.2[a]	39.09	8.69	39.69	9.04
$Zn(C_7SO_2H_5)\ (C_2H_4O_2N)\ (H_2O)_2$	white	*	33.35	9.89	33.74	9.52
$Zn(C_7SO_2H_5)\ (C_3H_6O_2N)\ (H_2O)_2$	white	*	35.52	9.48	35.92	9.84
$Zn(C_7SO_2H_5)\ (C_5H_{10}O_2N)\ (H_2O)_2$	white	*	39.09	8.69	39.39	9.04

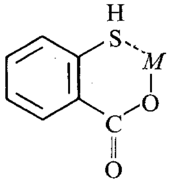
[a] Measured in *DMF*

* Insoluble in ethanol or *DMF*

Table 2. *Significant inrared bands* (cm^{-1}) *of the ternary complexes (*b *broad)*

Co(II)-*TSA*-gly	Co(II)-*TSA*-ala	Co(II)-*TSA*-val	Cu(II)-*TSA*-gly	Cu(II)-*TSA*-ala	Cu(II)-*TSA*-val	Zn(II)-*TSA*-gly	Zn(II)-*TSA*-ala	Zn(II)-*TSA*-val	Assignment
3 400 b	3 400 b	3 450 b	3 450 b	3 450 b	3 450 b	3 400 b	3 400 b	3 400 b	ν_{CH}
3 200 b	3 200 b	3 200 b	3 050 b	3 050 b	3 050 b	3 050 b	3 000 b	3 030	ν_{NH_2}
2 525	2 525	2 525	2 525	2 535	2 520	2 560	2 540	2 539	ν_{SH}
1 675	1 675	1 675	1 660	1 660	1 652	1 670	1 670	1 675	$\nu_{COO\text{-antisym.}}$
1 538	1 530	1 538	1 520	1 520	1 520	1 520	1 520	1 520	$\nu_{NH_2\text{-deformation}}$
1 412	1 412	1 422	1 412	1 420	1 412	1 410	1 422	1 412	$\nu_{COO\text{-sym.}}$
475	480	475	500	500	505	505	505	505	ν_{-M-N}
340	340	340	335	335	335	338	338	338	ν_{M-O}
290	290	290	285	285	285	280	280	280	ν_{M-S}

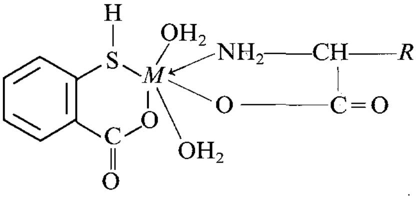
as shown in Table 1. The S—H stretching frequency band appearing at 2 516 cm^{-1} in the infrared spectrum of the free thiosalicylic acid is shifted to higher or less energies in the spectra of all complexes (2 560–2 520 cm^{-1}). This reveals that coordination through the unionised S—H group is achieved in all these complexes. This result is consistent with the formulation suggested by the micro-analyses results (Table 1) in which thiosalicylic acid appears to function as a mono-carboxylate. A convincing evidence for this behaviour can be attained from the high *pKa* value of the S—H group (9.52) relative to that of the COOH group (5.44) for thiosalicylic acid [3, 4]. However, the observed shift in the ν_{SH} to higher energies on complexation can be attributed to the high mesomeric interaction in the six membered chelated ring, which is formed in the complex in the presence of metal ion. Further remarkable similarities are observed among the ternary complexes in the absorption regions due to the amino and the carboxyl groups which are found to occur respectively in (a) 3 200–3 030 cm^{-1} (ν_{NH_2}), 1 538–1 520 cm^{-1} (NH_2 deformation) and (b) 1 675–1 652 cm^{-1} (antisymmetric carboxylate stretching vibrations) 1 422–1 410 cm^{-1} (symmetric carboxylate stretching vibrations). It should be mentioned that the appearance of the antisymmetric carboxylate stretching vibration in the range 1 675–1 652 cm^{-1} is consistent with the ionised and not the unionised carboxylate group being coordinated to the metal ion. This is substantiated by the results of the chemical analysis of the solid complexes (Table 1). Careful examination of the far infrared absorption spectra of the ternary complexes clearly display the *M*—N, *M*—O and *M*—S stretching vibrations in the ranges 505–475 cm^{-1}, 340–335 cm^{-1} and 290–280 cm^{-1} respectively [5–7].



Electronic Spectra of the Cu(II)-*Thiosalicylic Acid—Amino Acid Ternary Complexes*

The visible electronic spectra in *DMF* solutions of Cu(II)-amino acid exhibit a broad band centered at 735 nm with molar extinction coefficient 38 l^{-1} cm^{-1} mol^{-1} suggesting a pseudo tetrahedral structure of the Cu-amino acid complex [8]. On the other hand the *DMF* solution of the ternary Cu(II)-amino acid-thiosalicylic acid complex exhibits a shift in the main visible band of the Cu(II)-amino acid complex to lower energies (λ_{max} = 655 nm, ε_{max} = 45 l^{-1} cm^{-1} mol^{-1}). This indicates a tetragonally distorted structure for the ternary complex prepared by complexation of the Cu(II) amino acid complex with thiosalicylic acid as a secondary ligand [9].

Based on the above discussion, one can deduce the fact that both the monovalent anions of amino and thiosalicylic acid are coordinated to the metal ion as N, O and S, O bidentate ligands respectively, where five and six chelated rings are formed. The structure of the 1 : 1 : 1 ternary complexes studied in this investigation can be represented schematically as below:



M = Co^{2+}, Cu^{2+}, Zn^{2+}
R = H (gly); CH_3 (ala); $CH(CH_3)_2$ (val)

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