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Synthesis, Characterization and Antimicrobial Activity of Thiomalates of Mn(II), Fe(II) and Co(II)

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Four metal thiomalates of Mn(II), Fe(II) and Co(II) have been isolated and characterized by elemental, spectral (IR) and thermogravimetric analyses. The antibacterial and antifungal activities of thiomalic acid have been found to be appreciably enhanced on complexation with the metal ions especially in case of compounds of Mn(II) and Co(II).

INTRODUCTION

Thiomalic acid (TMA) is a versatile ligand having soft sulphur of the sulphydryl group and hard oxygens of the two carboxylate groups and its complexes with a number of metal ions including those of Mn(II)[1,2], Fe(II)[3] and Co(II)[2,4-6] have been reported in solution phase only. In this paper we report the preparation, characterization and antimicrobial activity of Mn(II), Fe(II) and Co(II) thiomalate complexes.

EXPERIMENTAL

$MnCl_2 \cdot 4H_2O$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and thiomalic acid used were of analytical reagent (AR) grade the solvents were purified and redistilled before use.

Preparation of Complexes

(a) *1 : 2 Mn(II)–TMA; Mn* $(C_4H_5O_4S)_2$: 0.01 mole of $MnCl_2 \cdot 4H_2O$ was dissolved in about 30 ml of methanol. To this 0.02 mole of methanolic solution of TMA was added dropwise and with constant stirring. The clear solution thus obtained was concentrated over water bath to *ca.* 15 ml. Then benzene was added to separate out the buff coloured complex. This was filtered and washed with benzene and dried over fused $CaCl_2$ in vacuo (yield: *ca.* 65%).

(b) *1 : 2 Fe(II)-TMA*; $Fe(C_4H_5O_4S)_2$: 0.01 mole of ferrous ammonium sulphate was dissolved in about 25 ml of distilled water, to which 1 ml of conc. H_2SO_4 was added to prevent hydrolysis. Hydrogen was passed to this solution to reduce any Fe^{3+} present. De-gassed aq. ammonia solution was added while passing H_2 in the Fe(II) solution to precipitate $Fe(OH)_2$. This precipitate was filtered and washed with water saturated with H_2. Then de-gassed solution of TMA was added (0.02 mole) to dissolve the $Fe(OH)_2$ precipitate. The resultant clear solution was concentrated to about 15 ml under vacuo. Now methanol was added to separate the yellowish complex. This was filtered, washed with methanol and dried over fused $CaCl_2$ in vacuo (yield: *ca.* 30%).

(c) *1:1 and 1:2 Co(II)-TMA Complexes*: (i) *Co*($C_4H_4O_4S$): $CoCl_2{\cdot}6H_2O$ (0.01 mole) was dissolved in about 20 ml of water and to this a saturated solution of Na_2CO_3 (calculated amount) was added to precipitate $CoCO_3$. This was filtered and washed with water several times. Now this precipitate was transferred to a beaker containing aqueous TMA (> 0.01 mole) solution. This resulted in a clear brown coloured solution. This was concentrated to about 25 ml and then methanol was added to separate a brown complex which was filtered, washed with methanol and dried over fused $CaCl_2$ in vacuo (yield: *ca.* 95%).

(ii) *Co*$(C_4H_5O_4S)_2$: 0.01 mole of $CoCl_2{\cdot}6H_2O$ and 0.02 mole of TMA were dissolved in methanol separately. TMA solution was added to Co(II) solution dropwise and with constant stirring. The solution thus obtained was concentrated to about 20 ml and a little benzene was added to it. This was left overnight when reddish brown crystals of the complex separated. These were filtered, washed with benzene and dried over fused $CaCl_2$ in vacuo (yield: *ca.* 90%).

RESULTS AND DISCUSSIONS

The S–H stretching vibration in case of free TMA around 2560 cm^{-1} disappears on complexation with Fe(II) and Co(II) thiomalates, indicating involvement of —SH group in coordination. This fact is further supported by shifting of the C–S stretching frequencies towards lower wave numbers (i.e., < 660 cm^{-1}). The rather weak and diffused bands in the range of 320–200 cm^{-1} have been assigned as $\nu_{M\text{-}S}$ as reported in literature[7(a),8]. The band at about 1700–1685 cm^{-1} indicates the presence of at least one —COOH group in the original protonated state in the complex. Microtitration of aq. suspension of $Fe(C_4H_5O_4S)_2$ with NaOH indicated that all the four —COOH groups remain intact in the complex (i.e., deprotonation does not occur). The presence of only one such —COOH in case of $Co(C_4H_4O_4S)$ and two in $Co(C_4H_5O_4S)_2$ was also similarly established. The simultaneous linkage of metal ion with S of —SH group and oxygen of one of the —COOH groups has been reported in cases of thiomalates of Zn(II), Cd(II), Pb(II) and Hg(II) as well by other workers[9]. The IR spectrum of $Mn(C_4H_5O_4S)_2$ reflects a different behaviour. The S–H band in this thiomalate appears at *ca.* 2540 cm^{-1} indicating thereby that sulphydryl group in not involved in the bonding with the metal ion. The lowering of this frequency in the complex may be attributed to the involvent of —SH group in hydrogen bonding and/or weakening of the bond within the group as a result of coordination of the —COOH group attached to the same carbon atom as the sulphur. The asymmetric and symmetric COOH stretching frequencies of TMA at

1680 cm^{-1} and 1415 cm^{-1} are found to be lowered suggested that coordination has occurred through oxygen atoms. The $\nu_{M\text{-}O}$ appears at about 323 cm^{-1} as reported for other complexes[7(b)] of Mn(II). Similar type of linkage of metal ions has also been reported[10] for Mg, Ba, Sr and Ca where carboxylate groups of TMA are involved in bonding and sulphydryl group remains free. However, microtitration of the complex against NaOH indicated the presence of two protonated —COOH groups.

TABLE 1

ANALYTICAL DATA FOR METAL-THIOMALATE COMPLEXES

Complex	Analysis found (Calcd.)			Metal
	C	H	S	
$Mn(C_4H_5O_4S)_2$	27.44 (27.18)	3.86 (2.83)	16.14 (18.12)	15.24 (15.55)
$Fe(C_4H_5O_4S)_2$	25.84 (27.11)	2.82 (2.82)	15.67 (18.07)	15.98 (15.76)
$Co(C_4H_4O_4S)$	21.18 (23.18)	1.48 (1.93)	13.23 (15.45)	27.80 (28.45)
$Co(C_4H_5O_4S)_2$	24.01 (26.88)	3.00 (2.80)	15.34 (17.92)	16.44 (16.50)

Furthermore, the broad absorption in the region of OH stretching vibrations with submaximas reflects the polymeric nature of all these compounds due to hydrogen bonding between —COOH groups of neighbouring molecules.

Thermal Studies

The complexes start decomposing at about 60–120° and evolution of H_2O vapours and/or H_2S is observed. In case of $Mn(C_4H_5O_4S)_2$ the final product formed beyond 480°, correspond to a total weight loss of *ca.* 73% and the product is chemically identified as MnO_2 (Fig. 1) (theoretical weight loss *ca.* 75%).

The thermal study of $Fe(C_4H_5O_4S)_2$ shows a weight loss of *ca.* 56–60% at 260°–480° which may be due to the formation of $FeSO_4$ (calculated weight loss about 57%); however, the weight loss from *ca.* 520° onward increases to *ca.* 70%, which is probably due to partial oxidation of ferrous sulphate. Such formation of $FeSO_4$ during thermal studies of this complex may be promoted due to FeS linkage as shown from the IR studies.

The $Co(C_4H_4O_4S)$ starts losing weight at about 100° and continues upto 300° when a final product corresponding to total weight loss of *ca.* 55% is formed. This final product is chemically identified as CoS (calculated weight loss *ca.* 56%). In case of $Co(C_4H_5O_4S)_2$, also, the weight loss starts at about 60° and the same final product (CoS) is formed via three-step decomposition at 420° corresponding to total weight loss of about 78% (theoretical *ca.* 75%). The intermediates could not be identified because of very low range of stability. Thus, the formation of CoS in both the Co(II) thiomalates supports the conclusion drawn from IR studies that Co(II) is linked to S atom of —SH group in TMH molecule.

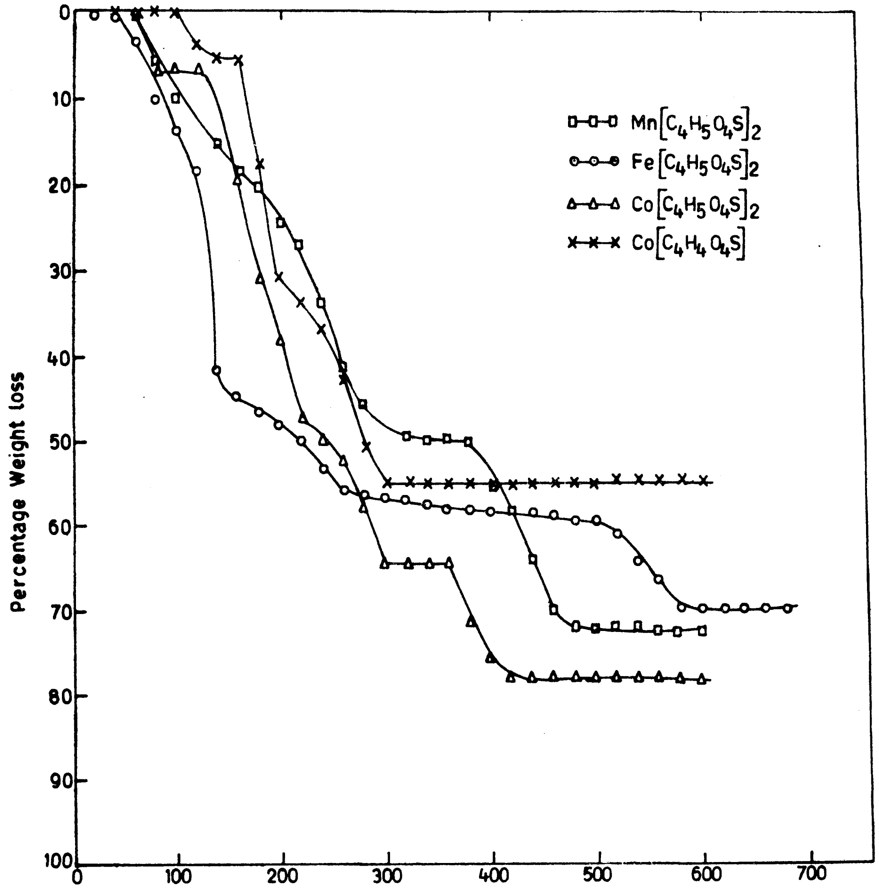

Fig. 1. TG curves for metal-thiomalates.

The conclusions arrived at from IR and thermal studies are that TMA molecules are linked to Mn(II) through oxygen, and Fe(II) and Co(II) through sulphur and oxygen both can also be explained theoretically on the basis of hard and soft nature of metal ions. Mn(II) is a hard species and hence, has overriding preference for coordination with oxygen whereas Fe(II) and Co(II) being borderline species may combine with oxygen as well as sulphur.

Antimicrobial Activities

The Mn(II), Fe(II) and Co(II) thiomalates were tested for their antimicrobial activity against gram-positive (*Staphylococcus aureous*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria and *Candida albicans* fungus by neat samples and serial plate dilution method[11]. The minimum inhibitory concentration (MIC) of these compounds as well as ligand are reported in Table 2. Results clearly establishes an appreciable enhancement of the antibacterial property of TMA on complexation with Mn(II) and Co(II) which are within therapeutic limits, an aspect which warrants further investigations.

TABLE 2

MIC Values (μg/ml) OF METAL-THIOMALATES AND TMA

Compound	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*
TMA	1000	500	500	**
$Mn(C_4H_5O_4S)_2$	500	**	62.5	62.5
$Fe(C_4H_5O_4S)_2$	*	*	*	*
$Co(C_4H_5O_4S)$	62.5	62.5	62-5	62.5

*Not active

**Active as neat sample only.

$Co(C_4H_4O_4S)$ could not be tested for its activity because of its insolubility in water, alcohol and DMF.

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