

## Preparation & characterisation of Co(II), Cu(II) and Fe(III) Complexes of Tetraoxalylurea

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**Summary:** Tetraoxalylurea and tetraoxalylthiourea have been synthesised. Co(II), Cu(II) and Fe(III) complexes have been prepared in different media and their structures were proposed on the basis of elemental analysis and IR measurements.

### Introduction

The reaction between urea and aliphatic dibasic acids depends upon the molar ratio of the reactants and the experimental conditions employed. At fusion condition, the dark infusible mass produced is said to be polymeric<sup>1</sup>. On the other hand, if reflux condition is employed and at molar ratio less than 1:4 (urea : dibasic acid), acid imide, acid di-imide and various condensation products are obtained. However at 1:4 molar ratio (urea: dibasic acid), the tetrafunctional compound is obtained.

The tetrabasic compound "tetrasuccinylurea" was recently incorporated in the preparation of modified polyester-type resins of improved film durability<sup>2</sup>.

This article is mainly concerned with the reaction of urea or thiourea with oxalic acid (OA) aiming to produce tetrafunctional products [tetraoxalylurea (TO urea) and tetraoxalyl-thiourea (TO thiourea)]. Also their ability to form various metal complexes is investigated.

### Materials & Methods

All chemicals used throughout this work were of the purest grade available. The metals salts  $\text{CoCl}_2$ ,  $\text{CuCl}_2$  and  $\text{FeCl}_3$  are of the chemically pure grade and are the products of B.D.H., England.

#### *Preparation of TO urea and TO thiourea (I & II):*

TO urea (I) and TO-thiourea (II) were prepared by refluxing a mixture of urea or thiourea (1 moles), OA (4 moles) and 150 ml xylene in Dean & Stark apparatus till the

theoretical amount of water was collected. The solid obtained was washed with xylene followed by recrystallisation from water and dried at  $50^\circ\text{C}$  in vacuo (Table 1). The yield percentages of I and II were found to be 71.8% and 94.9% and melting points of  $129-131^\circ$  and  $135-136^\circ\text{C}$  respectively.

#### *Preparation of metal complex (Ia-g & IIa)*

A solution of the anhydrous metal halide (0.02 mole) in 50 ml solvent was added dropwise to a solution of I and II (0.01 mole) in the same solvent. The mixture was refluxed for 3 hr. The product was filtered under nitrogen atmosphere, washed with absolute ethanol and dried in vacuo. The yield ranged between 70-100%. The analytical data of the complexes obtained are included in table 1.

Elemental analysis were carried out in the micro-analytical laboratories of El-Nasr Pharmaceutical Company and Cairo University. Cobalt and copper were determined complexometrically by EDTA titration. Iron was determined gravimetrically as oxide while the chloride was estimated using Volhard's method<sup>3</sup>. Water of crystallisation was estimated by heating at  $140^\circ\text{C}$  under vacuum till constant weight.

Physical measurements were conducted using Unicam SP 1200 and 8000 spectrophotometers. The molecular weights were determined according to Beckmann's method<sup>4</sup>.

### Results & Discussion

Recently TS urea was prepared by refluxing urea

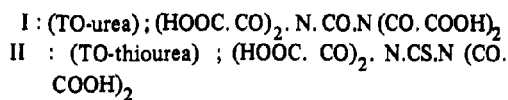
Table 1. Characteristics of Compounds I, II &amp; Their Metal Complexes\*

No.	medium	colour	M	Analysis (%) Reqd/Found				Formula
				Cl	C	H	N	
I	xylene	white	—	—	21.95	4.06	5.69	H <sub>4</sub> A.8 H <sub>2</sub> O
					20.98	5.16	5.63	
Ia	ethanol	pale	18.27	—	31.58	3.72	4.33	ACo <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub>
		purple	18.50		13.18	3.09	4.20	
Ib	water	pale	22.07					ACo <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>
		purple	22.37					
Ic	DMF	pale	19.38	23.36				H <sub>4</sub> ACo <sub>2</sub> Cl <sub>4</sub>
		purple	19.13	22.98				
Id	ethanol	bluish-	19.39					ACu <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub>
		green	18.76					
Ie	water	bluish-	23.39					ACu <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>
		green	25.88					
If	DMF	pale	20.58	23.01				H <sub>4</sub> ACu <sub>2</sub> Cl <sub>4</sub>
		blue	19.98	22.74				
Ig	ethanol	yellow	16.64	31.65**				H <sub>4</sub> AF <sub>3</sub> Cl <sub>6</sub>
		green	15.88	31.96				
II	xylene	white	—	—	21.25	3.93	5.51	H <sub>4</sub> B.8 H <sub>2</sub> O
					21.84	4.39	4.98	
IIa	ethanol	pale	17.40	—	30.00	3.54	4.13	BCo <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub>
		purple	17.82		12.89	3.13	2.34	

\* where H<sub>4</sub>A & H<sub>4</sub>B represent I : C<sub>9</sub>N<sub>2</sub>O<sub>13</sub> and II : C<sub>9</sub>N<sub>2</sub>O<sub>12</sub>S respectively, and M represents the metal.

\*\* ionisable chlorine % Reqd/Found = 21.10/20.96 and  
attached chlorine % Reqd/Found = 10.55/11.00

with succinic acid in xylene. The amount of water liberated was taken as a criterion for the termination of the reaction. Similarly, TO-urea and TO-thiourea were prepared under identical experimental conditions. Structures I and II are suggested for these compounds and are supported by the following considerations:



- (i) Acid value determination, Reqd/Found : 645/666 and 617/627 mg KOH for I & II respectively.
- (ii) Amount of water liberated, Reqd/Found : 18.0/21.6 and 18.0/20.0 ml for I & II respectively.
- (iii) Elemental analysis (table 1).
- (iv) Molecular weight determination, Reqd/Found: 348/360 and 364/370 for I & II respectively.
- (v) Potentiometric titration of I indicated that the dissociation constants of the four protons of TO urea are : pK<sub>1</sub> = 2.85 ; pK<sub>2</sub> = 3.75 ; pK<sub>3</sub> = 6.65 and pK<sub>4</sub> = 10.25

(vi) IR spectra show the characteristic bands of the various groups present.

Reaction of I & II with metal halides:

The reaction of I with 2 mole of anhydrous  $\text{CoCl}_2$  depends upon the solvent employed. Ia, Ib and Ic were obtained when absolute ethanol, water or DMF was used as a solvent respectively. After purification, these products analysed as :

$\text{Co}_2\text{C}_9\text{N}_2\text{O}_{13}(\text{C}_2\text{H}_5\text{OH})_4$  (Ia) ;  $\text{Co}_2\text{C}_9\text{N}_2\text{O}_{13}(\text{H}_2\text{O})_4$  (Ib) and  $\text{Co}_2\text{C}_9\text{H}_4\text{N}_2\text{O}_{13}\text{Cl}_4$  (Ic)

Washing of Ic with water leads to the formation of Ib as indicated by the presence of chloride ions in the filtrate.

Similarly, TO urea reacted with anhydrous  $\text{CuCl}_2$  in absolute ethanol, water or DMF as a medium to yield Id, Ie and If respectively. Elemental analysis suggested the formulae:  $\text{Cu}_2\text{C}_9\text{N}_2\text{O}_{13}(\text{C}_2\text{H}_5\text{OH})_4$  (Id) ;  $\text{Cu}_2\text{C}_9\text{N}_2\text{O}_{13}(\text{H}_2\text{O})_4$  (Ie) and  $\text{Cu}_2\text{C}_9\text{H}_4\text{N}_2\text{O}_{13}\text{Cl}_4$  (If)

The iron complex of TO urea (Ig) was prepared in absolute ethanol. Analytical data suggest :  $\text{Fe}_2\text{C}_9\text{H}_4\text{N}_2\text{O}_{13}\text{Cl}_6$  (Ig).

UV spectrum of Ig showed the characteristic absorption of the Fe-O bond at  $375\text{ cm}^{-1}$ . Treatment of Ig with  $\text{AgNO}_3$  resulted in the precipitation of 4 equivalent moles of  $\text{AgCl}$  indicating that only ionic chlorine atoms are present outside the complex. On the other hand, treatment of Ig with  $\text{NaOH}$  followed by neutralisation with  $\text{HNO}_3$  prior to the addition of  $\text{AgNO}_3$  resulted in the precipitation of 6 equivalent moles of  $\text{AgCl}$ . Both treatments indicated that the molecule contains two attached chlorine atoms in the inner sphere of the complex ion and 4 ionizable chlorine atoms outside the sphere.

In addition, the cobalt complex of TO thiourea (IIa) was prepared in ethanol and elemental analysis data suggest the formula :  $\text{Co}_2\text{C}_9\text{N}_2\text{O}_{12}\text{S}(\text{C}_2\text{H}_5\text{OH})_4$  (IIa).

It is noteworthy to mention that lower values of carbon percentages of the various metal complexes were observed and are attributed to the formation of metal

carbides<sup>5</sup>.

Similar type of complex compounds were recently prepared and evaluated as pigments and showed promising results<sup>6</sup>.

IR measurements showed the following observations:

- i. Metal-free compound (I & II) show a strong carbonyl band at  $1730$  and  $1720\text{ cm}^{-1}$  respectively which is attributed to the presence of the uncoordinated carboxyl group. Those belonging to EDTA<sup>7</sup> and TS-urea appear in the region  $1750 - 1550\text{ cm}^{-1}$ .
- ii. The strong carbonyl band of I & II disappeared in the spectra of their metal complexes and instead, a strong band appearing in the region of  $1650 - 1580\text{ cm}^{-1}$  which may due to the formation of  $\text{COO} \dots \text{M}$  bond.
- iii. The spectra of the different metal complexes show a band in the region  $1400 - 1300\text{ cm}^{-1}$  which is attributed to the coordinated oxalate groups. This is in agreement with Foracous's work<sup>8</sup> who stated that CO stretching bands of the coordinated oxalate groups appearing in the  $1500 - 1200\text{ cm}^{-1}$  region for many oxalate complexes. In addition, their spectra also show the metal-oxygen band at  $820 - 735\text{ cm}^{-1}$  region.
- iv. Most of the spectra of I, II and their metal complexes show a broad band in the region of  $3280 - 3200\text{ cm}^{-1}$  corresponding to the O-H stretching of water of hydration of alcohol molecules.
- v. The spectra of Ic & Ig show the metal-chloride band at  $495$  and  $540\text{ cm}^{-1}$  respectively. On the other hand, the spectra of II & IIa show the C-S band at  $1460$  and  $1410\text{ cm}^{-1}$  respectively.

Complete structure elucidation of the various metal complexes and their application in the analytical field are still under investigation.

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