Preparation & Characterisation of Fe(III), Co(II) and Cu(II) Complexes of Tetrasuccinylurea.

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Summary: Tetrasuccinylurea (TS urea) has been synthesised and its chemical reactions have been studied. Fe(III), Co(II) and Cu(II) complexes of TS urea have been prepared and their structures proposed on the basis of elemental analysis, IR and electronic spectral data.

Introduction

The reaction between urea and aliphatic polybasic acids has not been extensively studied. Fusion of urea with phthalic acid or the anhydride in presence of metal salts leads to the formation of the well-known phthalocyanines[1]. However, if aliphatic acids are employed, a dark infusible mass is obtained.[2] Recently, the tetrabasic compound (tetraoxalylurea) was prepared upon refluxing urea with oxalic acid at appropriate molar ratio[3]. This article is mainly concerned with the reaction of urea with succinic acid (SA) with a view to producing the tetracarboxylic compound tetrasuccinylurea (TS urea). Also its ability to form various metal complexes is investigated.

Materials & Methods

All chemicals used throughout the work were of Analar grade. The metal salts were the products of B.D.H., England.

Preparation of urea/SA condensation products (I - IV): A mixture of urea, SA and xylene (150 ml) was placed in Dean & Stark apparatus. The reaction mixture was allowed to reflux till the theoretical amount of water was collected. The solid obtained was washed with xylene followed by recrystallisation from a suitable solvent (Table 1).

Preparation of TS urea derivatives (IVa, b): A mixture of TS urea (1 mole), hydrazine or urea (4 mole) and xylene (150 ml) was refluxed in Dean & Stark apparatus till no more water liberated. The reaction mixture was filtered hot and the solid was washed with water and ethanol in the case of hydrazine derivative (IVa) and with acetone in case of urea derivative (IVb) Table 1).

Preparation of metal complexes (IVc-f): Anhydrous metal halides were first prepared.[4] A solution of the halide in 50 ml absolute ethanol was added dropwise to a solution of TS urea (1 mole) in 100 ml absolute ethanol containing KOH (4 mole) with continuous stirring. The reaction mixture undergoes colour change and a solid substance precipitates out. After complete addition of the metal halide, the mixture was refluxed for 1 hr. The product was filtered under nitrogen atmosphere, washed with absolute ethanol and dried in vacuo. The analytical data of the complexes are listed in Table 2.

Reaction of the cobalt complex with $AgNO_3$ (IVg-h): The cobalt complex of TS urea in 50 ml absolute ethanol was reacted with $AgNO_3$ in the molar ration of 1:4 and 1:2. The reaction mixture was stirred for 16 hr, the solid obtained was isolated and washed with ethanol. Their analyses are included in Table 2.

Elemental analyses were carried out at the microanalytical laboratories of El-Nasr Pharmaceutical Company and Cairo University. Cobalt and copper contents were determined complexometrically by EDTA titration. Iron was determined gravimetrically as oxide while the chloride was determined using Volhard's method[5].

Physical measurements were conducted using Unicam SP 1200 and 8000 spectrophotometers, NMR spectra were recorded using a Varian S60T Spectrophotometer. Molecular weight determination was carried out according to Beckmann's method.

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Table 1. Characteristics of Different Urea/SA Condensation Products

Compound	Reactant molar ratio				m.p.	Yield	Analysis (%) Reqd (Found)		
	Urea		SA		(°C)	(%)	C	H	N
I ($C_4H_8N_2O_2$)	1	:	1 2	or	>250*	83.3	41.38 (42.51)	6.90 (7.20)	24.14 (22.63)
II ($C_4H_5NO_2$)	1	:	1 2	or	115	65.5	48.47 (48.79)	5.05 (5.21)	14.14 (14.16)
III ($C_{12}H_{16}N_2O_8$)	1	:	3		105–108	72.8	45.57 (47.78)	5.06 (5.04)	8.86 (8.56)
IV ($C_{17}H_{20}N_2O_{13}$)	1	:	4		106–107	71.8	44.35 (43.63)	4.35 (4.69)	6.09 (6.02)
IVa ($C_{17}H_{28}N_{10}O_9$)	1	:	4		265	72.0	39.54 (41.18)	5.42 (5.14)	27.13 (25.74)
IVb ($C_{21}H_{28}N_{10}O_{13}$)	1	:	4		230–240	77.0	40.12 (38.23)	4.45 (6.26)	22.29 (25.67)

*undergo decomposition

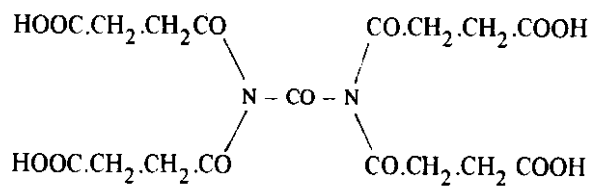
Results & Discussion

SA reacts with urea under the fusion conditions to produce a dark infusible mass which is said to be polymeric[2]. However, when the reaction was performed under refluxing conditions, the product obtained depended upon the molar ratio of the reactants. At molar ratios 1:1 and 1:2 (urea : SA), succinidiamide (I) and succinimide (II) were obtained and identified. At 1 : 3 molar ratio, a white crystalline product resulted which upon crystallisation from hot xylene showed a m.p. of 105-108° and a acidity of 440 mg KOH. Elemental analyses and IR measurements suggested structure (III):

$HOOC.(CH_2)_2.CONHCO.(CH_2)_2.CONHCO.(CH_2)_2.COOH$

The formation of (III) is belived to proceed by direct attack of SA on the formed succinidamide (I).

When the reaction was carried out in molar ratio 1:4, a white substance was obtained. On crystallisation from acetone its analysis corresponded to $C_{17}H_{20}N_2O_{13}$. Structure (IV) is suggested for this compound.



(IV) Tetrasuccinylurea (TS Urea)

Table 2. Analytical Results for TS urea-Metal Complexes

Compound*	Colour	Analysis (%) Reqd (Found) M	Cl	C**	H	N
IVc	Violet	13.53 (15.40)	16.28 (15.80)	23.39 (14.80)	1.83 (2.50)	3.21 (3.60)
($K_4Co_2YCl_4$)						
IVd	Red	8.86 (10.08)				
($K_2CoH_2YCl_2$)						
IVe	Blue-Green	14.41 (17.62)	16.12 (19.20)	23.16 (17.10)	1.82 (2.80)	3.18 (2.50)
($K_4Cu_2YCl_4$)						
IVf	Red-brown	12.39 (13.54)	16.40 (19.84)			
($K_4Fe_2YCl_4$)						
IVg	Grey	12.07 (9.08)				
($K_4Co_2Y(NO_3)_4$)						
IVh	Grey	8.21 (8.54)				
$K_2Co\,H_2Y(NO_3)_2$)						

** Low carbon percentage is attributed to the formation of metal carbides (5).

* TS urea is represented by H_4Y

This structure is supported by the following evidences:

i. Acid value determination (reqd 487; found 501 mg KOH)
ii. Water liberated (reqd 18; found 17. 5 ml)
iii. Molecular weight (reqd 460; found 472)
iv. Formation of hydrazine and urea derivatives (IV and (Vb, Table 1).
v. Potentiometric titration with 0.4 M KOH indicated that compound (IV) is a tetrabasic acid with dissociation constnats pK_1 = 3.10; pK_2 = 3.95; pK_3 = 7.60 and pK_4 = 10.45
vi. IR spectrum showed the characteristic stretching frequencies of the various groups present while NMR spectrum showed the signal characteristic for the methylene protons at δ = 2.86 ppm with spin-spin coupling constant j_{H-H} = 7 Hz
vii. Reduction of compound (IV) with Zn/HCl or alkaline hydrolysis yielded SA.

Reaction of TS urea with metal halides:

Trial reactions of TS urea (1 mole) with anhydrous $CoCl_2$ (1 or 2 mole) were unsucessful when performed in absolute ethanol in acidic medium. However when the reaction was carried out at pH 7-10 using alcoholic KOH solution, a violet crystalline compound was obtained. After purification, the product analysed as K_4Co_2 $(C_{17}H_{16}N_2O_{13})Cl_4$ (IVc). UV visible spectrum of (IVc) showed two absorption bands at 250 and 650 nm due to the carbonyl

Table 3. Infrared Assignments of TS urea and Its Complexes

Compound							
IV	IVc	IVd	IVe	IVf	IVg	IVh	Assignment
1740s 1380s		1700w					Uncoordinated carboxylic gr.
	1600s	1630s	1630s	1585s	1570s	1585s	Coordinated carboxylic gr.
	380s	370s	390s	380s	340s	380s	υ M – O
	3400br	3400br	3400br	3400br	3400br	3400br	υ O-H hydrate
1280w	1280m	1280m	1285m	1290m	1280m	1280m	υ C – N
1410m	1410s	1410s	1400m	1420s	1400s	1400s	υ CH_2 –CO

All bands in cm^{-1} and s, m, w and br represent strong, medium, weak and broad bands respectively.

group and tetrahedral co(II) complex respectively[4]. In addition, when the molar ratio of the reactatns as 1:1, the product isolated analysed as $K_2Co(C_{17}H_{18}N_2O_{13})Cl_2$, (IVd).

Similarly, TS urea reacted with anhydrous $CuCl_2$ or $FeCl_3$ in the presence of KOH to yield (IVe) as a bluish-green solid and suggested the formulas $K_4Cu_2(C_{17}H_{16}N_2O_{13})Cl_4$ (IVe) and $K_2Fe_2(C_{17}H_{16}N_2O_{13})Cl_4$ (IVf).

Reaction of (IVc) and (IVd) with $AgNO_3$: The chlorine atoms in (IVc) and (IVd) are replaceable as shown by reaction with $AgNO_3$. according to equations:

$$IVc + AgNO_3 \xrightarrow{\text{ethanol}} \underset{(IVg)}{K_4Co(C_{17}H_{16}N_2O_{13})(NO_3)_4} + 4\,AgCl$$

$$IVd + 2\,AgNO_3 \xrightarrow{\text{ethanol}} \underset{(IVh)}{K_2Co(C_{17}H_{18}N_2O_{13})(NO_3)_2} + 2AgCl$$

EDTA and TS urea belong to the same symmetry group and accordingly the same distribution pattern would be expected in the spectra of both compounds[7-9]. Table 3 lists the important infrared assignments of TS urea and its complexes. A strong band at 1740 cm^{-1} is attributed to the υCOO of agreement with assignment of υ COO in EDTA and its complexes in the range 1750 – 1550 cm^{-1} 10. On the other hand, the spectra of TS urea-metal complexes showed a strong band between 1630 and 1570 cm^{-1} which is attributed to the coordinated COO. . ..M.

The band at 1740 cm^{-1} (υ COO of TS urea) disappears in the spectra of TS urea complexes while a strong band appears at 1600 cm^{-1}. IR spectrum of (IVd) shows two carbonyl bands. a stronger band appearing between 1630 and 1585 cm^{-1} which may be attributed to the coordinated carboxyl groups and a weaker band at 1700 cm^{-1} which is associated with the free carboxyl group. Only one carbonyl band appears in the spectrum of (IVc).

Complexing of the carboxyl groups shifts the carbonyl band towards lower frequencies while the band associated with the free carboxyl group is shifted towards higher frequencies.

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