

КРАТКИЕ СООБЩЕНИЯ

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ZINC CITRATE WITH ALKALI METAL AND AMMONIUM CATIONS:
CRYSTAL STRUCTURE OF $K_4[Zn(Citrate)_2]$ © 2010 Y. Kim¹, H.G. Koo², D.H. Shin², L.O. Park³, J.H. Lee⁴, H.G. Jang^{4*}, C. Kim^{2*}¹Department of Chemistry and Nano Science, Ewha Womans Univeristy, Seoul 120-750, South Korea²Department of Fine Chemistry, and Eco-Product and Materials Education Center, Seoul National University of Technology, Seoul 139-743, South Korea³Tongil Obstetrics and Gynecology, 56-3 Banpo-Dong, Seocho-Gu, Seoul 137-040, South Korea⁴Department of Chemistry, Korea University, Seoul 136-701, South Korea

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In the crystal of $K_4[Zn(Citrate)_2]$, two citrate anions coordinate Zn(II) cation with octahedral geometry in the $[Zn(Citrate)_2]^{4-}$ complex anion, and the charge is balanced by four potassium ions. Crystal data: monoclinic, $P2_1/c$, $a = 8.502(2)$ Å, $b = 13.210(3)$ Å, $c = 8.942(2)$ Å, $\beta = 113.132(4)^\circ$, $V = 923.5(4)$ Å³, $Z = 2$, $R = 0.0229$.

Key words: zinc citrate, synthesis, crystal structure, citric acid.

Citric acid is a tricarboxylic acid which can undergo different degrees of deprotonation [1–3] and thus can form various reaction products with alkali and transition metals such as sodium [1, 4], potassium [5], magnesium [6], iron [7, 8], zinc [9], nickel [10], manganese [11], cobalt [12], vanadium [13] with different molar ratios. Its most important role is the solubilization of metal ions and thus enhancement of their bioavailability and subsequent absorption by biological tissues. This prominent function of the citric acid is directly related to its metal-chelating capacity, which is manifested in its multimodal coordination to biologically significant metal ions, zinc and nickel. Acrodenitis enteropathica is a genetic disorder of zinc metabolism [2, 14]. The signs of zinc deficiency appear when infants with the disorder are fed with cow's milk or can be alleviated by human milk, even though cow's milk generally contains more zinc than human milk. We presume that this disorder could be caused by different binding ability of citrate ion to zinc metal and alkali metals such as sodium and potassium. Therefore, the need to understand (a) the relative binding interaction of the zinc, sodium and potassium ions with the citrate ligand and (b) the ability of the citrate ion as an organic cofactor to efficiently mobilize these essential elements and enhance its availability to biological sites prompted us to investigate the competitive reaction between zinc and alkali metals, sodium and potassium, to citrate ion in aqueous solutions. We report herein the synthesis, isolation, and structural characterization of the first mononuclear zinc citrate complex containing potassium cation in aqueous solution.

Experimental. The $(NH_4)_4[Zn(Citrate)_2]$ (**1**) and $[Na_3(Citrate)] \cdot 5.5H_2O$ (**2**) were reported previously [2, 4], but we synthesized them and re-collected data for the crystal structures. The parameters of the crystal structures were very similar to those previously reported.

Preparation of $K_4[Zn(Citrate)_2]$ (3**):** 33.4 mg (0.016 mmol) of $ZnCl_2$ and 465.8 mg (0.16 mmol) of citric acid were dissolved in 15 ml water and then pH of the solution was adjusted to 7.0 by adding KOH. The solution was carefully layered by 15 ml MeOH.

X-Ray Diffraction Analysis: The X-ray diffraction data for the two compounds were collected on a Bruker SMART APX diffractometer equipped with monochromated MoK_α ($\lambda = 0.71073$ Å)

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Crystallographic Data for Compounds **1**, **2** and **3**

Parameter	1 ^a	2 ^b	3
Empirical formula	C ₁₂ H ₂₆ N ₄ O ₁₄ Zn	C ₆ H ₅ Na ₃ O _{12.5}	C ₁₂ H ₁₀ K ₄ O ₁₄ Zn
Formula weight	515.74	346.07	599.97
Temperature, K	170(2)	293(2)	293(2)
Wavelength, Å	0.71073	0.71073	0.71073
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	8.7566(16)	16.456(3)	8.502(2)
<i>b</i> , Å	13.494(3)	26.429(4)	13.210(3)
<i>c</i> , Å	9.0546(17)	6.4345(10)	8.942(2)
β, deg.	113.459(3)	90	113.132(4)
Volume, Å ³	981.5(3)	2798.4(7)	923.5(4)
<i>Z</i>	2	4	2
Density (calc.), g/cm ³	1.745	1.638	2.158
Absorption coeff., mm ⁻¹	1.334	0.236	2.308
Crystal size, mm	0.25 × 0.20 × 0.10	0.20 × 0.15 × 0.15	0.15 × 0.10 × 0.10
Reflections collected	5318	16735	5040
Independent reflections	1907 [<i>R</i> (int) = 0.1101]	3476 [<i>R</i> (int) = 0.1016]	1805 [<i>R</i> (int) = 0.0309]
Data/restraints/parameters	1907 / 8 / 178	3476 / 0 / 203	1805 / 0 / 146
GOOF on <i>F</i> ²	1.002	0.819	0.924
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0925	<i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.1213	<i>R</i> ₁ = 0.0229, <i>wR</i> ₂ = 0.0505
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0418, <i>wR</i> ₂ = 0.0936	<i>R</i> ₁ = 0.1299, <i>wR</i> ₂ = 0.1283	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0512
Largest peak and hole, e·Å ⁻³	0.66 and -0.75	0.47 and -0.27	0.30 and -0.32

^a Practically identical to previously reported [2].

^b Practically identical to previously reported [4].

source. Each crystal was mounted on a glass fiber. The data on reflection intensities were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V6.12 [15]. All hydrogen atoms were placed in calculated positions. Structural information for **3** was deposited at the Cambridge Crystallographic Data Center (CCDC reference number 628842). The crystallographic data for compounds **1**, **2** and **3** are listed in Table.

Results and Discussion. [Zn(Citrate)₂]⁴⁻ complex ion containing two triply ionized citrates has been reported, and the charge balance was achieved by four ammonium ions [2]. In the crystal of **1**, the zinc ion lies on an inversion center, octahedrally coordinated by two equivalent citrates. [Zn(Citrate)₂]⁴⁻ complex ions are indirectly cross-linked into a three-dimensional network through hy-

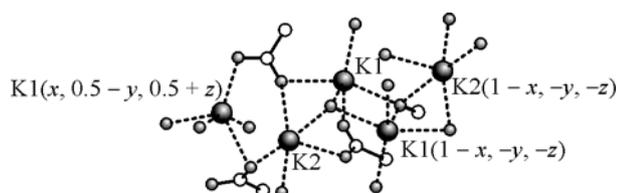
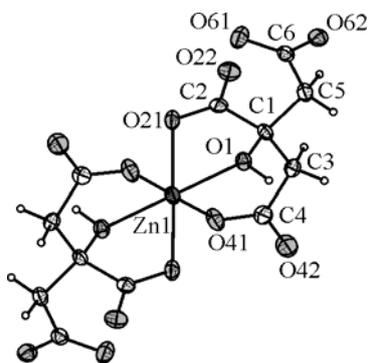
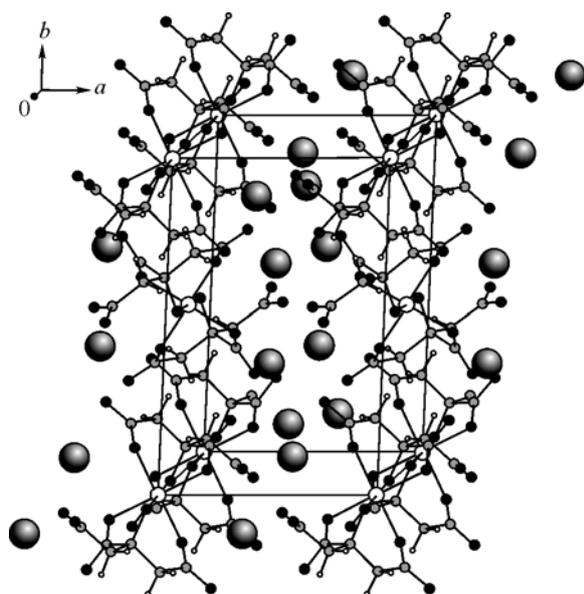
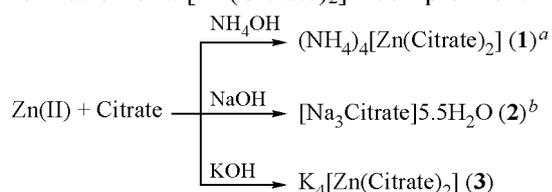


Fig. 1 (left). The structure of the [Zn(Citrate)₂]⁴⁻ anion in **3** with 50 % ellipsoids. Selected bond distances: Zn1—O21 2.093(2) Å, Zn1—O41 2.047(2) Å, Zn—O1 2.135(2) Å

Fig. 2 (right). The coordination geometry of K⁺ ions in **3**

Fig. 3. The unit cell contents of **3**

oxygen atoms of the citrate ion are hard, and they like hard sodium ions. The potassium and ammonium ions are slightly softer, so they are not directly coordinated by hard oxygen atoms of citrates and act just as counter cations. So, it seems to be important to select appropriate counter cation for the formation of a $[\text{Zn}(\text{Citrate})_2]^{4-}$ complex ion.



than those from zinc to acid oxygen atoms (2.047(2) and 2.093(2) Å). The $[\text{Zn}(\text{Citrate})_2]^{4-}$ complex anion of **3** is surrounded by K^+ ions. The K^+ ions of **3** are coordinated by oxygen atoms of citrate ions, yielding a coordination number of 5, with trigonal bipyramidal geometry (Fig. 2). Fig. 3 shows the unit cell contents of **3**.

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drogen bonds between oxygen atoms of citrates and ammonium hydrogen atoms.

In order to deeper investigate possible structures of zinc citrate ions, we have changed the counter cations balancing the charge from ammonium ions to sodium and potassium ions (see Scheme). If the sodium ion was used as a counter cation, citrates did not coordinate the zinc ion to form a zinc complex but yielded trisodium citrate 5.5-hydrate (**2**) whose structure was determined previously [4]. Final result is that the potassium ions can replace the ammonium positions in the crystal structures while the sodium ions can not act as a counter cation but can be directly coordinated by triply ionized citrate. The result could be explained by the hard-soft acid-base (HSAB). The

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