Coordination Polymers of CuII with the Ligand Pyrazine-2,3,5,6-tetracarboxylic Acid

Marion Graf, Helen Stoeckli-Evans*, and Claire Whitaker, and in part Pierre-Alain Marloni and Werner Marty

Abstract. The ligand pyrazine-2,3,5,6-tetracarboxylic acid in the presence of CuCl₂ and the buffers CH₂COO⁻/CH₃CO₂⁻, X = K⁺, Rb⁺, Cs⁺ and (CH₃COO)₂Mg/CH₂CO₂H, forms two quite different types of coordination polymers. With the monovalent K⁺, Rb⁺, or Cs⁺ buffer an almost right-angled dimeric unit is formed which polymerizes to form a zig-zag polymer \( [\text{Cs}_{2}\text{Cu}(pztc)_{2}2\text{H₂O} \cdot 9\text{H₂O}] \) \( \cdot \) (1). This 'dimerizes' about a center of symmetry to form a two-dimensional polymer sheet. With the divalent Mg²⁺ buffer a mononuclear unit polymerizes to form a quasi-linear polymer \( [\text{MgH}_2\text{O}_6(\text{Cu}(pztc)2\text{H}_2\text{O})2\text{H}_2\text{O}] \) \( \cdot \) (2). The X-ray crystal structures of 1 and 2 indicate that the Cu atom exists in two quite different coordination environments (NO₃ square pyramidal for 1 and N₂O₅ square planar for 2) and that the Cu-N(pyrazine) bond distances are much longer than normal.

Introduction

Pyrazine-2,3,5,6-tetracarboxylic acid ( pztc ) and its Na⁺, K⁺, and Ba²⁺ salts, as well as its Ag⁺ complex, have been known since the last century \{1\}. In the 80's the late Werner Marty suggested the possibility of forming quasi-linear coordination polymers with this potentially bis(tridentate) binucleating ligand and transition metal ions.

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Pyrazine-2,3,5,6-tetracarboxylic acid (= H₄pztc) and its Na⁺, K⁺, and Ba²⁺ salts, as well as its Ag⁺ complex, have been known since the last century [1-2]. In the 80’s the late Werner Marty suggested the possibility of forming quasi-linear coordination polymers with this potentially bidentate binucleating ligand and transition metal ions.

[1] J.D. Peterson, W.R. Murphy, R. Sahai, K.J. Brewer, R.R. Ruminski, *Coord. Chem. Rev.* 1985, 64, 261.
[2] P.J. Steel, *Coord. Chem. Rev.* 1990, 106, 227.
[3] W. Kaim, S. Kohlmann, *Inorg. Chem.* 1986, 25, 3306; ibid, 1987, 26, 68.
[4] S. Campagna, G. Denti, G. De Rosa, L. Sabatino, M. Ciano, V. Balzani, *Inorg. Chem.* 1989, 28, 2565.
[5] S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano, V. Balzani, *Gazz. Chim. Ital.* 1989, 119, 415.
[6] S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano, V. Balzani, *Inorg. Chem.* 1990, 29, 4750.
[7] G. Denti, S. Serroni, L. Sabatino, M. Ciano, V. Ricevuto, S. Campagna, *Gazz. Chim. Ital.* 1991, 121, 37.
[8] S. Ernst, V. Kasack, W. Kaim, *Inorg. Chem.* 1988, 27, 2714.
[9] S. Ernst, V. Kasack, W. Kaim, *J. Am. Chem. Soc.* 1990, 112, 173.
[10] W. Kaim, S. Kohlmann, *Inorg. Chem.* 1990, 29, 2909.
[11] S. Serroni, G. Denti, *Inorg. Chem.* 1992, 31, 4251.
[12] G. Denti, S. Serroni, S. Campagna, V. Ricevuto, A. Juris, M. Ciano, V. Balzani, *Inorg. Chem. Acta* 1999, 198-200, 307.
[13] P.W. Nebel, G. Huh, *Anal. Chem.* 1935, 513, 283.
[14] G. Clemo, *J. Soc. Chim. 1938*, 753.

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A number of structurally different polymeric materials have been obtained by reacting an aqueous solution of MCl₂ or MSO₄, where M = Mn²⁺, Fe²⁺, Co²⁺, and Zn²⁺, with 1 equiv. of H₄pztc and in other cases Mn²⁺, Cu²⁺, and Zn²⁺ salts with 1 equiv. of H₄pztc in the presence of a buffer [3]. The first structure of one such quasi-linear polymer from an aqueous solution, namely [(Fe(H₂pztc)·2H₂O)·2H₂O]ₙ, was published in 1986 [4]. It is isomorphous with the Co²⁺ and Zn²⁺ polymers produced under the same conditions [3]. The structures of a zig-zag Mn²⁺ polymer, produced under the same conditions, and the isomorphous Mn²⁺ and Zn²⁺ column type polymers, formed in the presence of a K⁺ buffer solution, will be published elsewhere [5]. Here, we wish to report on the X-ray crystal structures of the coordination polymers formed by the reaction of an aqueous solution of CuCl₂ with H₄pztc with the addition of a) the buffer CH₂CO₂X/CH₃CO₂H, X = K⁺, Rb⁺, Cs⁺ and b) the buffer (CH₃CO₂)₂Mg·CH₃CO₂H.

Results

Synthesis. The ligand H₄pztc is most easily obtained by Wolff's original synthesis [1][2]. Crystals of the pale green-blue polymer {Cs₄[Cuipztc]₂·2H₂O·9H₂O}ₙ (1), were obtained by slow cooling and evaporation of an aqueous 60° solution of CuCl₂ with H₄pztc to which was added a 2M solution of the equimolar buffer CH₂CO₂K/CH₂CO₂H. Upon changing the alkali metal from K⁺ to Rb⁺ to Cs⁺ the intensity of the colour and the stability of the crystals, which were isomorphous, increased. When left in air the crystals containing Cs⁺ lost water most slowly. Polymer {Mg(H₂O)₂[Cu(pztc)-2H₂O]·2H₂O}ₙ (2), crystallized as pale green-blue plates on cooling and slow evaporation of an aqueous 50° solution of CuCl₂ with H₄pztc to which had been added a 2m solution of the equimolar buffer (CH₂CO₂)₂Mg/CH₂CO₂H.

Structure of {Cs₄[Cuipztc]₂·2H₂O·9H₂O}ₙ (1). The basic unit of this polymer consists of a Cu-atom coordinated differently to two completely deprotonated pyrazinetetra-carboxylic acid anions. Each pyrazine ring is situated about a center of symmetry and they are inclined to one another by 83.3(5)°. This unit polymerizes to form a zig-zag polymer, Fig. 1. The coordination of the Cu-atom is best described as square-pyramidal with the Cu-atom displaced by 0.147(2) Å from the best plane through atoms N(21), O(W1), O(11), and O(21) [±0.078(3) Å] and in the

![Fig. 1. ORTEP [11] view of {Cs₄[Cuipztc]₂·2H₂O·9H₂O}ₙ (1). Bond distances Cu–O(11) 1.904(3), Cu–O(W1) 2.034(4), Cu–N(21) 2.139(3), Cu–O(21) 1.920(3), Cu–N(11) 2.329(4), Cu–O(W1') 2.599(4), Cu–Cu' 3.642(2) Å; bond angles O(11)–Cu–N(11) 77.75(12)°, O(11)–Cu–O(21) 174.78(14)°, O(11)–Cu–N(21) 100.20(13)°, O(11)–Cu–O(W1) 87.51(14)°, O(W1)–Cu–N(11) 96.27(13)°, O(W1)–Cu–O(21) 89.61(13)°, O(W1)–Cu–N(21) 164.60(14)°, O(21)–Cu–N(11) 106.92(13)°, O(21)–Cu–N(21) 81.62(12)°, N(11)–Cu–N(21) 98.38(13)°, Cu–O(W1)–Cu' 102.96(13)°.

Fig. 2. PLUTO [12] plot of the 2-D sheet of 1 formed in the ab plane. ■ Cu-atoms; the Cs⁺ cations and H₂O molecules of crystallization have been omitted for clarity.
**Structure of \( \{\text{Mg(H}_2\text{O})_6\}\{\text{Cu(pztc)}\cdot 2\text{H}_2\text{O}\}_\infty \) (2).** This quasi-linear polymer structure, Fig. 3, is very similar to that found for the neutral Fe\(^{II}\) polymer (4) Fig. 2). The basic unit consists of a Cu-atom, located on a center of symmetry, coordinated to the pyrazine N-atom and an oxygen of one carboxylic group on either side of a square plane. The coordination of the Cu-atom is square planar with the Cu-atom lying in the best plane through atoms N(1), O(1), N(1'), and O(1'), with atoms O(W1) and O(W1') occupying positions ±2.373(2) Å from the square plane. The non-coordinated carboxylic groups, involving O(3) and O(4), are inclined by −85.5(2)° to the best plane through the pyrazine ring. The polymer chains run parallel to the b-axis and are separated by the Mg hexahydrate cations and the H\(_2\)O molecules of crystallization, Fig. 4. The whole assembly is linked by an extensive H-bonding network involving the water molecules of the cation Mg hexahydrate (O(W1), O(W2), and O(W3)), the coordi-

The polymer chains themselves ‘dimerize’ about a center of symmetry forming Cu-OH\(_2\)...Cu bridges, with a Cu-Cu distance of 3.642(2) Å. In this way a two-dimensional sheet is formed in the ab plane, Fig. 2. The space between these sheets is occupied by the alkali-metal cations and the water molecules of crystallization. The coordinated H\(_2\)O molecules OW(1), the H\(_2\)O molecules of crystallization O(W2–6), and the O-atoms of the non-coordinated carboxylic groups, O(13), O(14) and O(23), O(24), are involved in an extensive H-bonding network which links the two-dimensional sheets. The shortest Cs...Cs distance is 4.150(1) Å (Cs(1)...Cs(1')), while the shortest Cs...O distance is 3.033(2) Å involving atoms Cs(1) and O(W4). There are two short contacts to Cs(1) involving atoms O(12) and O(21), 3.035 and 3.120 Å, respectively. There are four short contacts to Cs(2) involving atoms O(12), O(22), O(22'), and O(23); 3.093, 3.128, 3.135, and 3.170 Å, respectively.

The ORTEP (11) view of \( \{\text{Mg(H}_2\text{O})_6\}\{\text{Cu(pztc)}\cdot 2\text{H}_2\text{O}\}_\infty \) (2). Bond distances Cu–O(1) 1.901(1), Cu–N(1) 2.140(2), Cu–O(W4) 2.376(2) Å; bond angles O(1)–Cu–N(1) 98.61(6)°, O(1)–Cu–O(1') 180°, O(1)–Cu–O(W4) 88.43(6)°, N(1)–Cu–O(1') 81.39(6)°, N(1)–Cu–N(1') 180°, N(1)–Cu–O(W4) 92.59(6)°.

Fig. 3. ORTEP [11] view of \( \{\text{Mg(H}_2\text{O})_6\}\{\text{Cu(pztc)}\cdot 2\text{H}_2\text{O}\}_\infty \) (2). Bond distances Cu–O(1) 1.901(1), Cu–N(1) 2.140(2), Cu–O(W4) 2.376(2) Å; bond angles O(1)–Cu–N(1) 98.61(6)°, O(1)–Cu–O(1') 180°, O(1)–Cu–O(W4) 88.43(6)°, N(1)–Cu–O(1') 81.39(6)°, N(1)–Cu–N(1') 180°, N(1)–Cu–O(W4) 92.59(6)°.

Fig. 4. PLUTO [12] plot of the crystal packing in 2. ● Cu-atoms, □ Mg-atoms.

direction of atom N(11), itself displaced by 2.396(4) Å from the square plane. The non-coordinated carboxylic groups, involving O(13), O(14) and O(23), O(24), are inclined to the best planes through the pyrazine rings by 84.1(4)° and 82.3(4)°, respectively.
nated H₂O molecules O(W4), the water molecules of crystallization O(W5), and the O-atoms of the coordinated and non-coordinated carboxylic groups, O(2), O(3), and O(4).

Selected bond distances and bond angles are given in Figs. 1 and 3. The Cu–N(pyrazine) distances of 2.139(3) Å for 1 [2.127(2) Å for the K⁺ salt and 2.123(2) Å for the Rb⁺ salt] and 2.140(2) Å for 2, are significantly longer than the standard average value 2.024 Å [6] or those values observed for the mono and di-nuclear copper complexes formed with teta(2-piryld)pyrazine, where the same distance is 1.943(4) Å and 1.962(3) Å, respectively [7]. However, a similar distance, 2.135(5) Å, has been observed recently in a Cu₄ mononuclear complex of the new ligand dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate [8].

Conclusion

The ligand pyrazinetetracarboxylic acid normally coordinates in a bis(bidentate) fashion with first row transition metals and Zn. This is probably due to the large steric interaction that would arise between the adjacent carboxyl groups if the ligand coordinated in a bis(tridentate) fashion. Due to steric hindrance the non-coordinated carboxylic groups are twisted by 84°, on average, to the plane of the pyrazine rings. The coordination environment of the Cu-atom is N₂O₂ in both polymers, or more precisely NO₃ NO in 1 and N₂O₂ O₂ in 2. A number of different coordination polymer structures can be obtained firstly by varying the transition metal and secondly by varying the valency of the cation used to form the buffer. In our laboratory work is continuing on the synthesis of new di- and trita-substituted pyrazine ligands and on their ability to coordinate first row transition metals and zinc in order to produce new coordination polymers.

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Experimental

Synthesis of Pyrazine-2,3,5,6-tetracarboxylic Acid (H₄pztc). The ligand was synthesized by literature methods [1][2].

Synthesis of [Cu₄(C₆H₄O₂)₄(H₂pztc)·2H₂O]·9H₂O (1). An aq. soln. of CuCl₂·2H₂O (0.164 g, 0.97 mmol in 8 ml of H₂O) was added to an aq. soln. of H₄pztc (0.25 g, 0.97 mmol in 20 ml of H₂O) under N₂ at 60°. 15 ml of a 2 M AcOH/cesium acetate buffer (equimolar, pH = 6) was added and the soln. stirred. The deep green soln. was filtered and left to cool. After slow evaporation in air for a number of weeks, green-blue crystals were formed.

Synthesis of [Mg(H₂O)₄(Cu₂pztc)·2H₂O·2H₂O]·12H₂O (2). To a soln. of CuCl₂ (0.26 g, 1.94 mmol) dissolved in 20 ml of H₂O was added a soln. of H₄pztc (0.5 g, 1.94 mmol) in 20 ml of H₂O. The reaction mixture was stirred at 50° under N₂. To this 30 ml of a 2 M AcOH/Mg acetate buffer (equimolar) was added, bringing the pH to 4.8–5.0. The green soln. was stirred and left to cool to r.t. The soln. was filtered and allowed to evaporate slowly in air. After a number of weeks, green crystals were obtained.

X-Ray Crystal Structure Determinations. 1: [Cu₄(C₆H₄O₂)₄·2H₂O]·9H₂O, M₄ = 361.0, triclinic, P1, a = 9.400(4), b = 10.259(4), c = 10.685(4), α = 64.611(1)°, β = 75.771(1)°, γ = 69.6(4), V = 866.4(6) Å³, Z = 1, D₂ = 2.609 g cm⁻³, λ = 0.71073 Å, µ = 54.5 cm⁻¹, F(000) = 650, 3924 unique reflections, 3668 observed (I>2σI), R = 0.033, R₁ = 0.081, k = 0.002, S = 1.76. Max shift/sigma ratio 0.033, residual density (e/Å³) max. 1.94 near atom Cs(2), min –2.02.

2: [Cu₄(C₆H₄O₂)₄·2H₂O]·Mg(H₂O)₄·12H₂O, M₄ = 520.1, triclinic, P1, a = 6.019(1), b = 7.003(1), c = 11.183(2), α = 89.19(1)°, β = 74.618(1)°, γ = 89.83(1)°, V = 454.5(1) Å³, Z = 1, D₀ = 1.900 g cm⁻³, l = 0.71073 Å, µ = 13.3 cm⁻¹, F(000) = 267. 2080 unique reflections, 1755 observed (I>2σI), R = 0.028, R₁ = 0.041, k = 0.0015, S = 0.99. Max shift/sigma ratio 0.074, residual density (e/Å³) max. 0.45, min –0.81. Intensity data were collected at r.t. on a Stoe AED2 4-circle diffractometer using MoKα graphite monochromated radiation. Crystals of both 1 and 2 were covered with a thin layer of an epoxy resin. An empirical absorption correction was applied to structure 1 [9], transmission factors were max. 0.251 and min. 0.132. The structures were solved by Paterson and difference Fourier syntheses using the NRCVAX [10] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [10] are from [11]. The majority of H-atoms were located from difference maps. In 1 they were held fixed (Uiso = 0.075 Å²) while in 2 they were refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where w = 1/[σ²(F)² + k(F)²]. Atomic parameters and complete tables of bond distances and angles, for the isomorphous Cs⁺, Rb⁺, and K⁺ polymers,1 and the Mg⁺⁺ polymer 2, have been deposited with the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, England. The numbering schemes used are illustrated in the ORTEP-II [12] plots, Figs. 1 and 3; the packing diagrams were drawn using PLUTO [13], Figs. 2 and 4. Further details may be obtained from the author H. St. E.

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[1] L. Wolff, Ber. Dtsch. Chem. Ges. 1887, 20, 425.

[2] L. Wolff, Ber. Dtsch. Chem. Ges. 1893, 26, 721.

[3] P.-A. Marioni, Thése de Doctorat, Neuchâtel, 1986.