1643 observed [$I > 2.5\sigma(I)$], $R = 0.040$, $R_w =$ 0.056, $k = 0.001$, $S = 1.52$. Max. shift/sigma ratio 0.003, residual density (e/Å^3) max. 0.67, min. –0.34.

Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK$_\alpha$ graphite monochromated radiation and ω/Θ scans out to 50° in 2Θ. The structures were solved by direct methods or *Patterson* syntheses in the case of the metal complexes, using the NRCVAX [19] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [19] are from [20]. The majority of H-atoms were located from difference maps and refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where $w = 1/[\sigma^2(F_o) + k(F_o^2)]$. Crystals of the Fe complex **3** were twinned about the **c** axis. This preliminary structure analysis is rather unsatisfactory from the point of view of accuracy; the e.s.d.'s of the bond distances and angles are certainly underestimated. Further attempts will be made to improve this situation. Atomic parameters and complete tables of bond distances and angles for structures **1**, **2**, and **4** 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 [21] plots, *Figs. 1a, 2a, 3a*, and *4a*. *Figs. 1b, 2b, 3b*, and *4b* were drawn using PLUTO [22]. Further details may been obtained from *H. St.-E.*

Received: April 6, 1993

[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*, 1146.

[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. Chim. Acta* **1992**, *198–200*, 507.

[13] P.W. Neber, G. Huh, *Anal. Chem.* **1935**, *515*, 283.

[14] G. Clemo, *J. Chem. Soc.* **1938**, 753.

[15] K. Haarmann, Doctoral Thesis, University of Fribourg, 1991.

[16] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[17] F. Allen, S. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers, D.G. Watson, 'Cambridge Crystal Structure Data Base', *Acta Crystallogr., Sect. B* **1979**, *35*, 2331 (version Jan. 1993, as installed at ETH-Zürich).

[18] A. Neels, H. Stoeckli-Evans, to be published.

[19] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, P.S. White, 'NRCVAX', *J. Appl. Crystallogr.* **1989**, *22*, 384.

[20] 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, England, 1974, Vol. IV (Present distributor: Kluwer Academic Publishers, Dordrecht).

[21] C. K. Johnson, 'ORTEP-II', Report 5138, Oak Ridge National Laboratory, Oak Ridge, Tenessee, USA, 1976.

[22] W.D.S. Motherwell, W. Clegg, 'PLUTO', Program for Plotting Molecular and Crystal Structures, University of Cambridge, UK, 1978.
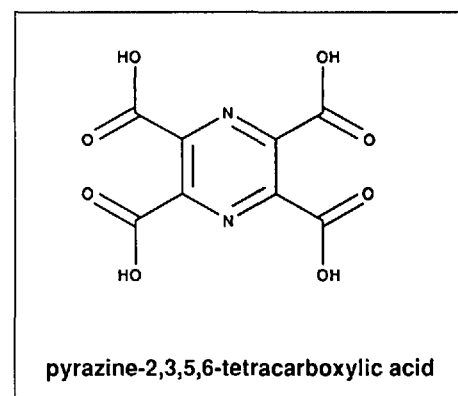
Coordination Polymers of Cu^{II} with the Ligand Pyrazine-2,3,5,6-tetracarboxylic Acid

Marion Graf, **Helen Stoeckli-Evans***, and **Claire Whitaker**, and in part **Pierre-Alain Marioni** and **Werner Marty**[†]

Abstract. The ligand pyrazine-2,3,5,6-tetracarboxylic acid in the presence of CuCl$_2$ and the buffers CH$_3$CO$_2$X/CH$_3$CO$_2$H, X = K$^+$, Rb$^+$, Cs$^+$ and (CH$_3$CO$_2$)$_2$Mg/CH$_3$CO$_2$H, 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 {Cs$_4$[Cu$_2$(pztc)$_2$2H$_2$O]·9H$_2$O}$_\infty$ (**1**). This 'dimerizes' about a center of symmetry to form a two-dimensional polymer sheet. With the divalent Mg^{2+} buffer a mononuclear unit polymerizes to form a *quasi-linear* polymer {Mg(H$_2$O)$_6$[Cu(pztc)2H$_2$O]·2H$_2$O}$_\infty$ (**2**). The X-ray crystal structures of **1** and **2** indicate that the Cu-atom exists in two quite different coordination environments (NO$_3$ square pyramidal for **1** and N$_2$O$_2$, 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 (= H$_4$pztc) and its Na$^+$, K$^+$, and Ba^{2+} salts, as well as its Ag^I 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 bis(tridentate) binucleating ligand and transition metal ions.

pyrazine-2,3,5,6-tetracarboxylic acid

*Correspondence: Prof. H. Stoeckli-Evans
Institut de Chimie
Université de Neuchâtel
Avenue de Bellevaux 51
CH–2000 Neuchâtel

1643 observed [$I > 2.5\sigma(I)$], $R = 0.040$, $R_w =$ 0.056, $k = 0.001$, $S = 1.52$. Max. shift/sigma ratio 0.003, residual density (e/Å^3) max. 0.67, min. –0.34.

Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK$_\alpha$ graphite monochromated radiation and ω/Θ scans out to 50° in 2Θ. The structures were solved by direct methods or *Patterson* syntheses in the case of the metal complexes, using the NRCVAX [19] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [19] are from [20]. The majority of H-atoms were located from difference maps and refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where $w = 1/[\sigma^2(F_o) + k(F_o^2)]$. Crystals of the Fe complex **3** were twinned about the **c** axis. This preliminary structure analysis is rather unsatisfactory from the point of view of accuracy; the e.s.d.'s of the bond distances and angles are certainly underestimated. Further attempts will be made to improve this situation. Atomic parameters and complete tables of bond distances and angles for structures **1, 2,** and **4** 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 [21] plots, *Figs. 1a, 2a, 3a,* and *4a. Figs. 1b, 2b, 3b,* and *4b* were drawn using PLUTO [22]. Further details may been obtained from *H. St.-E.*

Received: April 6, 1993

[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*, 1146.

[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. Chim. Acta* **1992**, *198–200*, 507.

[13] P.W. Neber, G. Huh, *Anal. Chem.* **1935**, *515*, 283.

[14] G. Clemo, *J. Chem. Soc.* **1938**, 753.

[15] K. Haarmann, Doctoral Thesis, University of Fribourg, 1991.

[16] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[17] F. Allen, S. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers, D.G. Watson, 'Cambridge Crystal Structure Data Base', *Acta Crystallogr., Sect. B* **1979**, *35*, 2331 (version Jan. 1993, as installed at ETH-Zürich).

[18] A. Neels, H. Stoeckli-Evans, to be published.

[19] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, P.S. White, 'NRCVAX', *J. Appl. Crystallogr.* **1989**, *22*, 384.

[20] 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, England, 1974, Vol. IV (Present distributor: Kluwer Academic Publishers, Dordrecht).

[21] C. K. Johnson, 'ORTEP-II', Report 5138, Oak Ridge National Laboratory, Oak Ridge, Tenessee, USA, 1976.

[22] W.D.S. Motherwell, W. Clegg, 'PLUTO', Program for Plotting Molecular and Crystal Structures, University of Cambridge, UK, 1978.
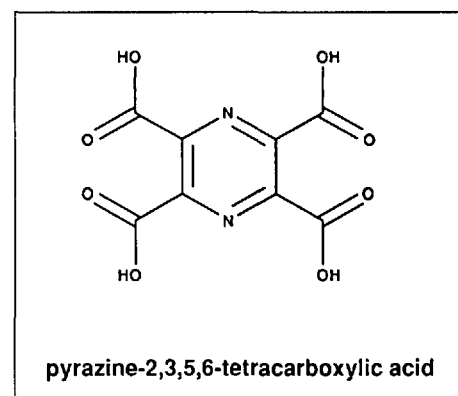
Coordination Polymers of Cu^{II} with the Ligand Pyrazine-2,3,5,6-tetracarboxylic Acid

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

Abstract. The ligand pyrazine-2,3,5,6-tetracarboxylic acid in the presence of CuCl$_2$ and the buffers CH$_3$CO$_2$X/CH$_3$CO$_2$H, X = K$^+$, Rb$^+$, Cs$^+$ and (CH$_3$CO$_2$)$_2$Mg/CH$_3$CO$_2$H, 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 {Cs$_4$[Cu$_2$(pztc)$_2$2H$_2$O]·9H$_2$O}$_\infty$ (**1**). This 'dimerizes' about a center of symmetry to form a two-dimensional polymer sheet. With the divalent Mg^{2+} buffer a mononuclear unit polymerizes to form a *quasi-linear* polymer {Mg(H$_2$O)$_6$[Cu-(pztc)2H$_2$O]·2H$_2$O}$_\infty$ (**2**). The X-ray crystal structures of **1** and **2** indicate that the Cu-atom exists in two quite different coordination environments (NO$_3$ square pyramidal for **1** and N$_2$O$_2$, 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 (= H$_4$pztc) and its Na$^+$, K$^+$, and Ba^{2+} salts, as well as its Ag^I 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 bis(tridentate) binucleating ligand and transition metal ions.

pyrazine-2,3,5,6-tetracarboxylic acid

Correspondence: Prof. H. Stoeckli-Evans
Institut de Chimie
Université de Neuchâtel
Avenue de Bellevaux 51
CH–2000 Neuchâtel

A number of structurally different polymeric materials have been obtained by reacting an aqueous solution of MCl_2 or MSO_4, where M = Mn^{II}, Fe^{II}, Co^{II}, and Zn^{II}, with 1 equiv. of H_4pztc and in other cases Mn^{II}, Cu^{II}, and Zn^{II} salts with 1 equiv. of H_4pztc in the presence of a buffer [3]. The first structure of one such *quasi-linear* polymer from an aqueous solution, namely $\{[Fe(H_2pztc) \cdot 2H_2O] \cdot 2H_2O\}_\infty$, was published in 1986 [4]. It is isomorphous with the Co^{II} and Zn^{II} polymers produced under the same conditions [3]. The structures of a *zig-zag* Mn^{II} polymer, produced under the same conditions, and the isomorphous Mn^{II} and Zn^{II} *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 $CuCl_2$ with H_4pztc with the addition of *a)* the buffer CH_3CO_2X/CH_3CO_2H, X = K^+, Rb^+, Cs^+ and *b)* the buffer $(CH_3CO_2)_2Mg/CH_3CO_2H$.

Results

Synthesis. The ligand H_4pztc is most easily obtained by *Wolff's* original synthesis [1][2]. Crystals of the pale green-blue polymer $\{Cs_4[Cu_2(pztc)_2 \cdot 2H_2O] \cdot 9H_2O\}_\infty$ (1), were obtained by slow cooling and evaporation of an aqueous 60° solution of $CuCl_2$ with H_4pztc to which was added a 2M solution of the equimolar buffer CH_3CO_2K/CH_3CO_2H. On 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 $\{Mg(H_2O)_6[Cu(pztc) \cdot 2H_2O] \cdot 2H_2O\}_\infty$ (2), crystallized as pale green-blue plates on cooling and slow evaporation of an aqueous 50° solution of $CuCl_2$ with H_4pztc to which had been added a 2M solution of the equimolar buffer $(CH_3CO_2)_2Mg/CH_3CO_2H$.

Structure of $\{Cs_4[Cu_2(pztc)_2 \cdot 2H_2O] \cdot 9H_2O\}_\infty$ (1). The basic unit of this polymer consists of a Cu-atom coordinated differently to two completely deprotonated pyrazinetetracarboxylic 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
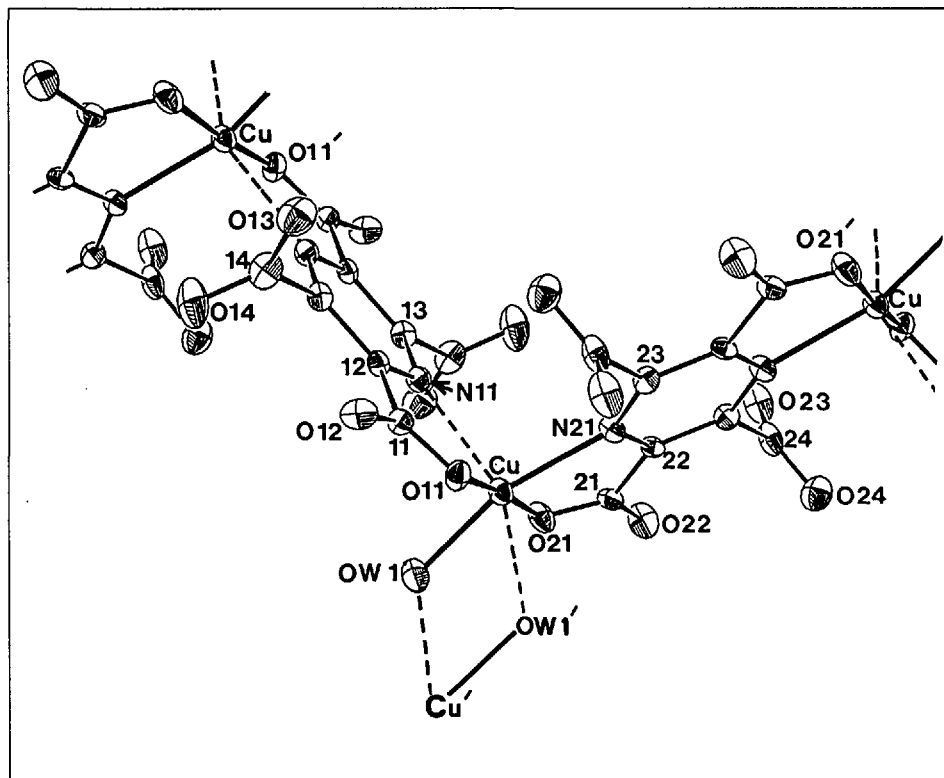

Fig. 1. *ORTEP* [11] *view of $\{Cs_4[Cu_2(pztc)_2 \cdot 2H_2O] \cdot 9H_2O\}_\infty$ (1).* Bond distances Cu–O(11) 1.904(3), Cu–O(W1) 2.034(4), Cu–N(21) 2.139(3), Cu–O(21) 1.920(3), Cu···N(11) 2.329(4), Cu···O(W1') 2.599(4), Cu···Cu' 3.642(2) Å; bond angles O(11)–Cu–N(11) 77.75(12)°, O(11)–Cu–O(21) 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)°.
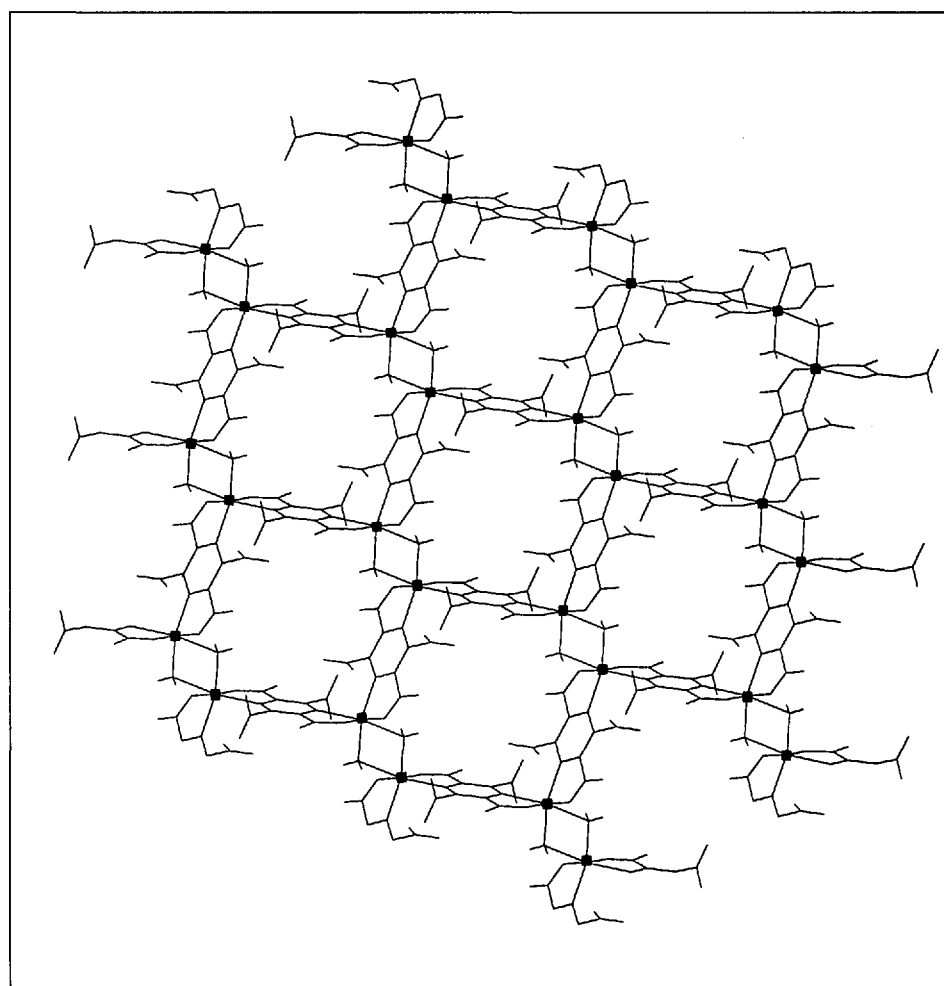

Fig. 2. *PLUTO* [12] *plot of the 2-D sheet of 1 formed in the* ab *plane.* ■ Cu-atoms; the Cs^+cations and H_2O molecules of crystallization have been omitted for clarity.
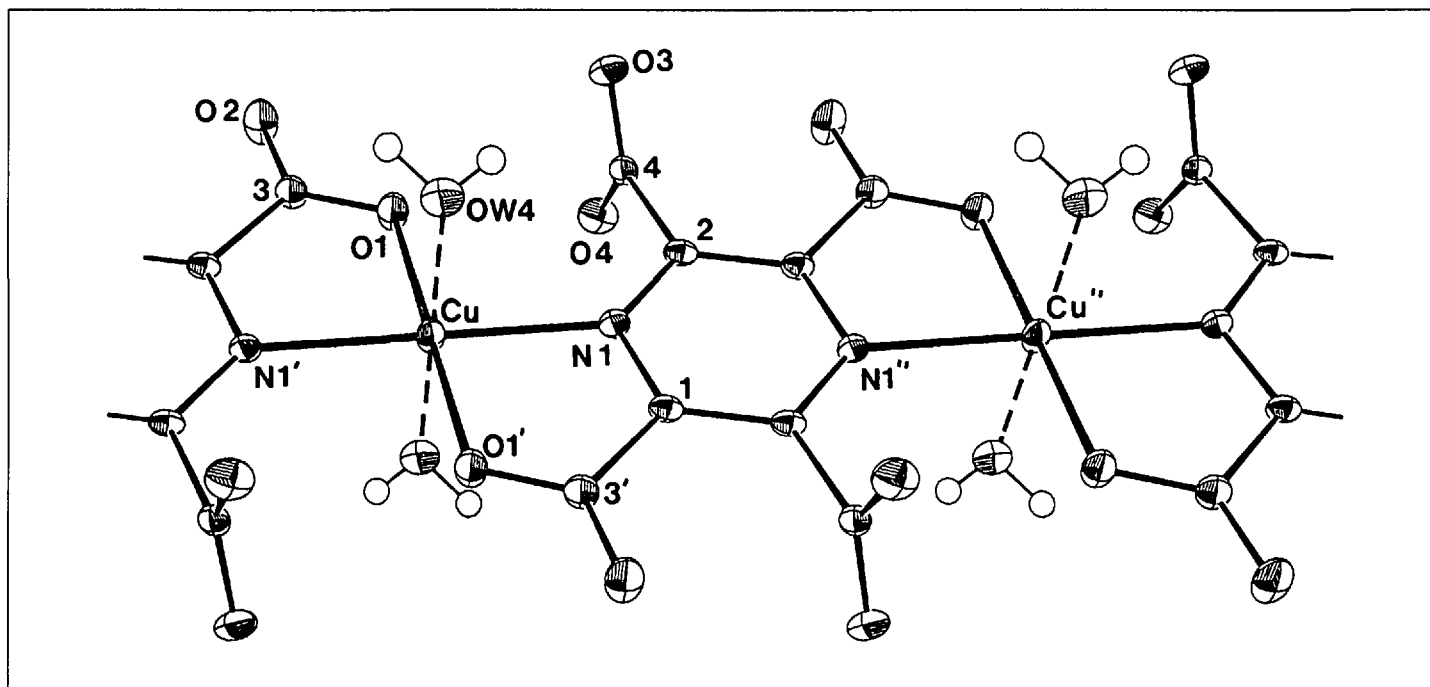
Fig. 3. *ORTEP* [11] *view of* $[Mg(H_2O)_6[Cu(pztc) \cdot 2H_2O] \cdot 2H_2O]_\infty$ (2). Bond distances Cu–O(1) 1.901(1), Cu–N(1) 2.140(2), Cu–O(W4) 2.376(2) Å; bond angles O(1)–Cu–N(1) 98.61(6)°, O(1)–Cu–O(1') 180°, O(1)–Cu–O(W4) 88.43(6)°, N(1)–Cu–O(1') 81.39(6)°, N(1)–Cu–N(1') 180°, N(1)–Cu–O(W4) 92.59(6)°
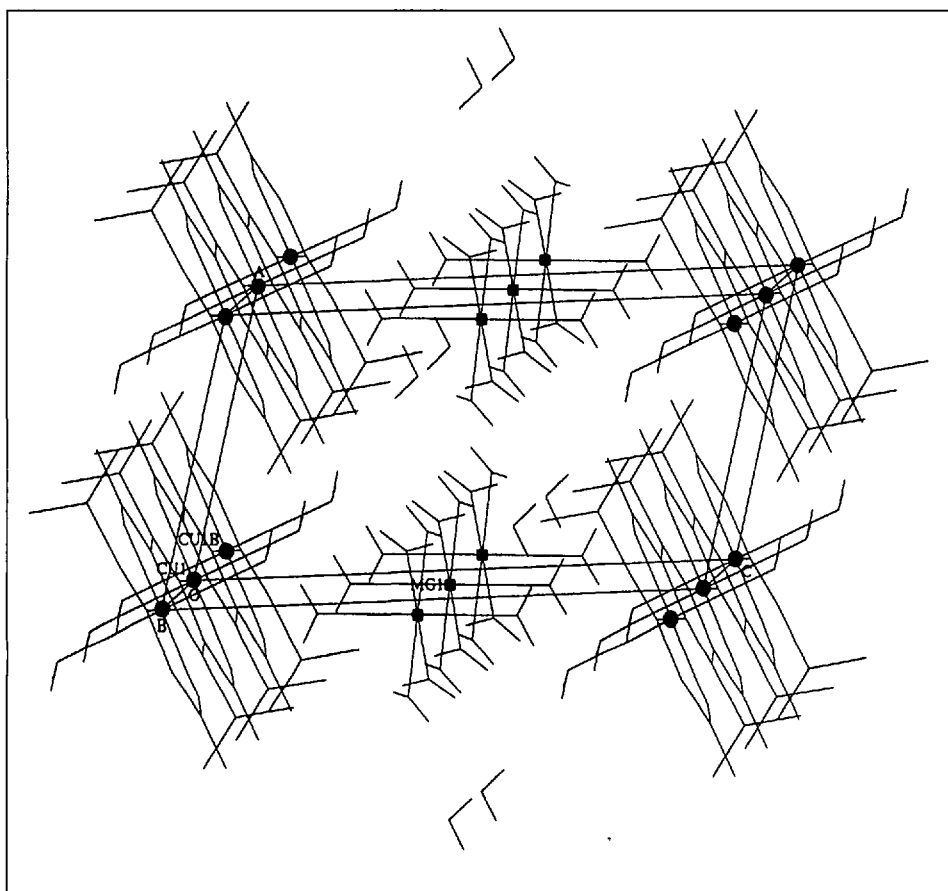

Fig 4. *PLUTO* [12] *plot of the crystal packing in* 2. ● Cu-atoms, ■ Mg-atoms.

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.

The polymer chains themselves 'dimerize' about a center of symmetry forming Cu–OH$_2\cdots$Cu bridges, with a Cu$\cdots$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$\cdots$Cs distance is 4.150(1) Å (Cs(1)$\cdots$Cs(1')), while the shortest Cs$\cdots$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.

Structure of $[Mg(H_2O)_6[Cu(pztc) \cdot 2H_2O] \cdot 2H_2O]_\infty$ (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-

nated H_2O 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 tetra(2-pyridyl)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 Cu^{II} 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 carbonyl 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 N_2O_4 in both polymers, or more precisely $NO_3 \cdot NO$ in **1** and $N_2O_2 \cdot O_2$ in **2**. A number of different coordination polymer structures can be obtained firstly by varying the transion 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 tetra-substituted pyrazine ligands and on their ability to coordinate first row transition metals and zinc in order to produce new coordination polymers.

Experimental

Synthesis of Pyrazine-2,3,5,6-tetracarboxylic Acid (H_4pztc). The ligand was synthesized by literature methods [1][2].

Synthesis of $\{Cs_4[Cu_2(pztc)_2 \cdot 2H_2O] \cdot 9H_2O\}_\infty$ (**1**). An aq. soln. of $CuCl_2 \cdot 2H_2O$ (0.164 g, 0.97 mmol in 8 ml of H_2O) was added to an aq. soln. of H_4pztc (0.25 g, 0.97 mmol in 20 ml of H_2O) under N_2 at 60°. 15 ml of a 2M 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 $\{Mg(H_2O)_6[Cu(pztc)\cdot 2H_2O] \cdot 2H_2O\}_\infty$ (**2**). To a soln. of $CuCl_2$ (0.26 g, 1.94 mmol) dissolved in 20 ml of H_2O was added a soln. of H_4pztc (0.5 g, 1.94 mmol) in 20 ml of H_2O The reaction mixture was stirred at 50° under N_2. To this 30 ml of a 2M 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**: $[Cu_2(C_{16}N_4O_{16}) \cdot 2H_2O]Cs_4 \cdot 9H_2O, M_r = 1361.0$, triclinic, $P\bar{1}$, $a = 9.400(4)$, $b = 10.269(4)$, $c = 10.685(4)$ Å, $\alpha = 64.61(1)°$, $\beta = 75.77(1)°$, $\gamma = 69.34(2)°$, $V = 866.4(6)$ Å^3, $Z = 1$, $D_x = 2.609$ g·cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 54.5$ cm^{-1}, $F(000) = 650$. 3924 unique reflections, 3668 observed $[I>3\sigma(I)]$, $R = 0.033$, $R_w = 0.081$, $k = 0.002$, $S = 1.76$. Max shift/sigma ratio 0.033, residual density (e/Å^3) max. 1.94 near atom Cs(2), min –2.02.

2: $[Cu(C_8N_2O_8) \cdot 2H_2O][Mg(H_2O)_6] \cdot 2H_2O$, $M_r = 520.1$, triclinic, $P\bar{1}$, $a = 6.019(1)$, $b = 7.003(1)$, $c = 11.185(2)$ Å, $\alpha = 89.19(1)°$, $\beta = 74.6181)°$, $\gamma = 89.83(1)°$, $V = 454.5(1)$Å^3, $Z = 1$, $D_x = 1.900$ g·cm^{-3}, $l = 0.71073$ Å, $\mu = 13.3$ cm^{-1}, $F(000) = 267$. 2080 unique reflections, 1755 observed $[I>3\sigma(I)]$, $R = 0.028$, $R_w = 0.041$, $k = 0.0015$, $S = 0.99$. Max shift/sigma ration 0.074, residual density (e/Å^3) max. 0.45, min –0.81. Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK_α 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 *Patterson* 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 ($U_{iso} = 0.075$ Å^2) while in **2** they were refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where $w = 1/[\sigma^2(F_0) + k(F_0^2)]$. Atomic parameters and complete tables of bond distances and angles, for the isomorphous Cs$^+$, Rb$^+$, and K$^+$ polymers **1**, and the Mg^{2+} 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 been obtained from the author *H. St.-E.*

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

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

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

[4] P.-A. Marioni, H. Stoeckli-Evans, W. Marty, H.-U. Güdel, A.F. Williams, *Helv. Chim. Acta* **1986**, *69*, 1004.

[5] P.-A. Marioni, W. Marty, H. Stoeckli-Evans, C. Whitaker, *Inorg. Chim. Acta* **1993**, submitted.

[6] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[7] M. Graf, B. Greaves, H. Stoeckli-Evans, *Inorg. Chim. Acta* **1993**, *204*, 239.

[8] Y. Wang, H. Stoeckli-Evans, to be published.

[9] *Stoe & Co.* 'REDU4 and EMPIR', Data-reduction and empirical absorption correction programmes. **1985**, *Stoe & Co.*, Darmstadt, Germany.

[10] E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, P. S. White, 'NRCVAX', *J. Appl. Crystallogr.* **1989**, *22*, 384.

[11] 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, England, 1974, Vol. IV (Present distributor Kluwer Academic Publishers, Dordrecht).

[12] C. K. Johnson, 'ORTEP-II', Report 5138, 1976, Oak Ridge National Laboratory, Oak Ridge, Tenessee, USA.

[13] W. D. S. Motherwell, W. Clegg, 'PLUTO', 1978, Program for plotting molecular and crystal structures, University of Cambridge, England.