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Structure of a Tripotassium Pyrroloquinoline Quinone Salt

Nobuhumi Nakamura, Takamitsu Kohzuma, Hiro Kuma and Shinnichiro Suzuki*

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

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Abstract

In $3K^+.C_{14}H_3N_2O_8^{3-}.4H_2O$, all three carboxyl groups of pyrroloquinoline quinone (PQQ; 4,5-dihydro-4,5-dioxo-1H-pyrrolo[2,3-f]quinoline-2,7,9-tricarboxylic acid) are in anion form to neutralize the three potassium cations. Each of the three potassium ions is closely coordinated to polar atoms of the PQQ^{3-} ions and waters of crystallization. Noticeable structural features within the crystal unit are the stacking of the PQQ^{3-} ions and the extensive network of hydrogen-bonding interactions.

Comment

PQQ is known as the coenzyme of a novel class of oxidoreductases (Duine, Frank Jzn & Verwiel, 1980; Duine & Frank Jzn, 1981). To understand its biological behavior, it is important to reveal the molecular structure and atomic charge distribution in the molecule. The structures of the 5-(2-oxopropyl) (Salisbury, Forrest, Cruse & Kennard, 1979; Cruse, Kennard & Salisbury, 1980) and 5-(2,4-dinitrophenylhydrazine) adducts of PQQ (van Koningsveld, Jansen, Jongejan, Frank Jzn & Duine, 1985) and the PQQ disodium salt (Ishida *et al.*, 1989) have been reported already. Ishida *et al.* (1989) demonstrated that the PQQ molecule possesses two sodium-binding sites. This is the first report on the crystal structure of the trianionic form of PQQ.
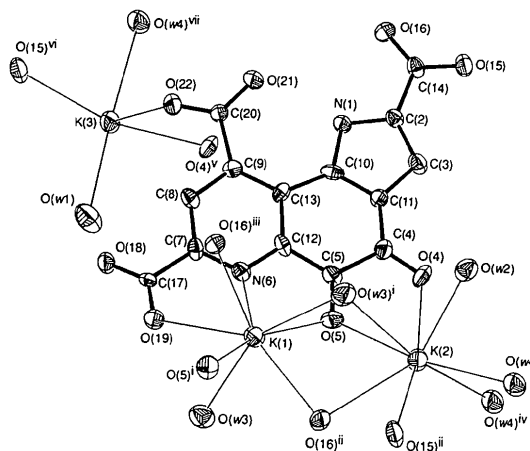

Fig. 1. Perspective view of $K_3(C_{14}H_3N_2O_8).4H_2O$ indicating the atom labeling. H atoms are omitted.

Fig. 1 shows a perspective drawing of the structure and indicates the atom-numbering scheme. In an earlier structural study of the PQQ disodium salt, PQQ formed dianions (PQQ^{2-}) (Ishida *et al.*, 1989). The charge on PQQ probably depends on the synthetic conditions. Since the present PQQ crystals were prepared under neutral conditions, the PQQ molecule formed trianions (PQQ^{3-}) with three carboxylate anion substituents. A comparison of the structures of PQQ^{3-} and PQQ^{2-} reveals very similar bond lengths and angles. The carboxylate C(2)—C(14) bond length of 1.498 (8) Å is also significantly shorter than the other two carboxylate C—C bond lengths [1.531 (8) and 1.552 (8) Å for C(7)—C(17) and C(9)—C(20), respectively]. This fact presumably results from the energetic stabilization of the carboxylate group through a resonance effect with the respective aromatic rings (Ishida *et al.*, 1989). Differences between PQQ^{2-} and PQQ^{3-} are manifest in the C(4)=O(4) bond lengths [1.204 (5) and 1.205 (6) Å in PQQ^{2-} (Ishida *et al.*, 1989) and 1.234 (8) Å in PQQ^{3-}]. The longer bond length in

PQQ^{3-} is due to the coordination of the O(4) atom to K(2) and K(3) ions.

The crystal structure analysis of the PQQ disodium salt demonstrated that the PQQ molecule possesses two metal-binding sites: a primary site in the pocket formed by the O(5), N(6) and O(19) atoms and a secondary site in the pocket formed by the O(4) and O(5) atoms (Ishida *et al.*, 1989). In the PQQ tripotassium salt, the two potassium cations [K(1) and K(2)] are also located at these sites. The other potassium cation [K(3)] is located at a novel site and is five-coordinate, with two PQQ^{3-} ions binding to it as monodentate ligands through O(4) and O(15), respectively. It seems that the location of the K(3) ion is favorable in view of the crystal packing.

The most interesting features in the crystal structure are the extensive network of hydrogen-bonding interactions and the stacking of the PQQ^{3-} ions. The stacking PQQ^{3-} ions form columns aligned along the crystallographic *b* axis. The closest interatomic distance between the PQQ^{3-} ions is 3.416 (8) Å {C(11)···C(13^v) [symmetry code: (v) $-x$, $1 - y$, $1 - z$]}. The hydrogen-bonding network and the stacking of the PQQ^{3-} ions play an essential role in stabilizing this crystal structure.

Experimental

Crystal data

K$_3$(C$_{14}$H$_3$N$_2$O$_8$).4H$_2$O
M_r = 516.54
Monoclinic
$P2_1/n$
a = 17.060 (2) Å
b = 7.088 (2) Å
c = 15.332 (2) Å
β = 91.76 (1)°
V = 1853.1 (7) Å^3
Z = 4
D_x = 1.852 Mg m^{-3}
D_m = 1.858 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 20 reflections
θ = 18–20°
μ = 7.33 mm^{-1}
T = 298 K
Needles
0.42 × 0.12 × 0.10 mm
Dark red
Crystal source: crystallization from H$_2$O/CH$_3$CN

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.7502, T_{max} = 0.9940
3364 measured reflections
2957 independent reflections
2127 observed reflections
[$I > 3\sigma(I)$]

R_{int} = 0.037
θ_{max} = 62.5°
h = −20 → 20
k = 0 → 8
l = 0 → 18
3 standard reflections monitored every 100 reflections
intensity variation: 4%

Refinement

Refinement on F
R = 0.056

w = $1/(\sigma^2 F + 0.0648|F|$ $+ 0.0002|F|^2)$

wR = 0.060
S = 1.23
2127 reflections
325 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{max}$ = 0.33
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
K(1)	−0.26077 (7)	0.1295 (2)	0.27651 (8)	2.36
K(2)	−0.08005 (7)	0.3300 (3)	0.10593 (8)	2.75
K(3)	−0.14302 (7)	0.3644 (3)	0.84090 (8)	2.83
O(4)	0.0340 (3)	0.4260 (7)	0.2566 (3)	3.41
O(5)	−0.1207 (3)	0.3875 (7)	0.2823 (3)	2.90
O(15)	0.2987 (3)	0.2586 (7)	0.4944 (3)	3.21
O(16)	0.2408 (3)	0.1914 (6)	0.6194 (3)	2.36
O(18)	−0.3297 (2)	0.2069 (7)	0.5826 (3)	2.53
O(19)	−0.3417 (2)	0.2014 (6)	0.4377 (3)	2.51
O(21)	0.0268 (3)	0.0846 (8)	0.6673 (3)	3.77
O(22)	−0.0886 (3)	0.0998 (7)	0.7261 (3)	3.07
N(1)	0.0940 (3)	0.2340 (7)	0.5360 (3)	1.98
N(6)	−0.1822 (3)	0.2693 (7)	0.4301 (3)	1.91
C(2)	0.1632 (3)	0.2718 (8)	0.4949 (4)	1.86
C(3)	0.1447 (3)	0.3298 (9)	0.4117 (4)	2.28
C(4)	0.0135 (3)	0.3713 (9)	0.3289 (4)	2.21
C(5)	−0.0754 (3)	0.3499 (9)	0.3419 (4)	2.11
C(7)	−0.2134 (3)	0.2193 (8)	0.5042 (4)	1.94
C(8)	−0.1671 (3)	0.1723 (8)	0.5771 (4)	2.01
C(9)	−0.0856 (3)	0.1798 (8)	0.5765 (4)	1.83
C(10)	0.0317 (3)	0.2656 (8)	0.4801 (4)	1.96
C(11)	0.0620 (3)	0.3279 (8)	0.4024 (4)	1.76
C(12)	−0.1041 (3)	0.2835 (8)	0.4270 (4)	1.90
C(13)	−0.0511 (3)	0.2402 (8)	0.4998 (4)	1.71
C(14)	0.2408 (3)	0.2384 (9)	0.5408 (4)	1.98
C(17)	−0.3028 (3)	0.2094 (8)	0.5083 (4)	1.60
C(20)	−0.0442 (3)	0.1191 (8)	0.6636 (4)	1.78
O(W1)	−0.2705 (3)	0.4165 (8)	0.7291 (3)	4.48
O(W2)	0.0408 (3)	0.0637 (7)	0.1189 (3)	3.07
O(W3)	−0.3640 (3)	0.4671 (7)	0.3025 (3)	3.33
O(W4)	−0.0056 (3)	0.2926 (7)	−0.0550 (3)	3.04

Table 2. *Selected geometric parameters* (Å)

K(1)—O(5)	3.008 (5)	O(16)—C(14)	1.250 (7)
K(1)—O(19)	2.913 (4)	O(18)—C(17)	1.242 (7)
K(1)—N(6)	2.852 (5)	O(19)—C(17)	1.253 (7)
K(1)—O(W3)	3.005 (5)	O(21)—C(20)	1.236 (8)
K(1)—O(5^i)	2.781 (5)	O(22)—C(20)	1.248 (7)
K(1)—O(16^{ii})	2.724 (4)	N(1)—C(2)	1.383 (7)
K(1)—O(16^{iii})	2.794 (4)	N(1)—C(10)	1.362 (7)
K(1)—O(W3^i)	2.736 (5)	N(6)—C(7)	1.317 (7)
K(2)—O(4)	3.052 (5)	N(6)—C(12)	1.339 (7)
K(2)—O(5)	2.842 (5)	C(2)—C(3)	1.368 (8)
K(2)—O(W2)	2.797 (5)	C(2)—C(14)	1.498 (8)
K(2)—O(W4)	2.821 (5)	C(3)—C(11)	1.414 (8)
K(2)—O(15^{ii})	2.716 (5)	C(4)—C(5)	1.544 (9)
K(2)—O(16^{ii})	3.073 (4)	C(4)—C(11)	1.411 (8)
K(2)—O(W3^i)	3.095 (5)	C(5)—C(12)	1.484 (8)
K(2)—O(W4^{iv})	3.158 (5)	C(7)—C(8)	1.389 (8)
K(3)—O(22)	2.752 (5)	C(7)—C(17)	1.531 (8)
K(3)—O(W1)	2.752 (5)	C(8)—C(9)	1.391 (8)
K(3)—O(4^v)	2.841 (5)	C(9)—C(13)	1.399 (7)
K(3)—O(15^{vi})	2.726 (5)	C(9)—C(20)	1.552 (8)
K(3)—O(W4^{vii})	2.841 (5)	C(10)—C(11)	1.385 (8)
O(4)—C(4)	1.234 (8)	C(10)—C(13)	1.465 (8)
O(5)—C(5)	1.209 (8)	C(12)—C(13)	1.448 (8)
O(15)—C(14)	1.244 (7)		

Symmetry codes: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x, -y, 1 - z$; (iv) $-x, 1 - y, -z$; (v) $-x, 1 - y, 1 - z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $x, y, 1 + z$.

PQQ was purchased from Ube Industries (Tokyo, Japan). PQQ was dissolved in KOH solution and the pH of the solution was then adjusted to 7.0 by the addition of HCl solution. The addition of CH_3CN to the solution yielded the crystals in a few weeks. The density was measured by flotation in CCl_4–$CH_2BrCH_2CH_2Br$. A crystal was sealed in a glass capillary for the collection of the diffraction data. The unit-cell parameters indicated a monoclinic crystal system and systematic absences indicated the space group. Lattice constants were obtained by least-squares refinement. Intensity data were collected with an ω-scan width of $(1.50 + 0.15\tan\theta)°$ and a scan speed of $4.0°$ min^{-1}. Data were corrected for Lorentz and polarization effects and for absorption.

The structure was solved by direct methods using *MULTAN78* (Main *et al.*, 1978) and refined by block-diagonal least squares using the program *HBLS-V* (Ashida, 1979). Anisotropic thermal parameters were refined for non-H atoms. The positions of the H atoms of PQQ were calculated on the basis of their molecular geometry. Difference Fourier syntheses calculated at intermediate stages of refinement showed maxima consistent with the expected positions of H atoms of water. H atoms were included with isotropic temperature factors in subsequent refinements. All computations were carried out on an ACOS 2020 computer at the Computation Center, Osaka University, and on an ACOS S-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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Dimeric Copper(II) 2-Methyl-2-phenylpropanoate Adducts with Water or 2,6-Lutidine and a Monomeric Copper(II) Triphenylacetate Adduct with 2,6-Lutidine

Toyoaki Fujita and Shigeru Ohba*

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

Megumi Nagamatsu and Tadashi Tokii

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

C. Fredrick Jury and Omar W. Steward

Department of Chemistry, Duquesne University, Pittsburgh, PA 15282, USA

Michinobu Kato

13–30, Takatorikita 4, Asaminami-ku, Hiroshima, 731-01, Japan

Abstract

The structures of diaquatetrakis(μ-2-methyl-2-phenylpropanoato-*O:O'*)dicopper(II), $[Cu(C_{10}H_{11}O_2)_2(H_2O)]_2$ (I), bis(2,6-dimethylpyridine)tetrakis(μ-2-methyl-2-phenylpropanoato-*O:O'*)dicopper(II) benzene solvate, $[Cu(C_{10}H_{11}O_2)_2(C_7H_9N)]_2.C_6H_6$ (II) and *trans*-bis(2,6-dimethylpyridine)bis(triphenylacetato-*O,O'*)copper(II), $[Cu(C_{20}H_{15}O_2)_2(C_7H_9N)_2]$ (III), have been determined by single-crystal X-ray diffraction. (I) and (II) are dinuclear Cu^{II} complexes having cage structures and the coordination geometries around the Cu atoms are square pyramidal in (I) and distorted trigonal bipyramidal in (II). The Cu⋯Cu distances are 2.589 (1) and 2.907 (1) Å for (I) and (II), respectively. The coordination geometry in the monomeric copper complex (III) is square planar. The $-2J$ values of (I) and (II) are 348 and 310 cm^{-1}, respectively.

Comment

The antiferromagnetic interaction in dimeric copper-(II) carboxylates decreases as the coordination geometry around the Cu atoms is distorted from square pyramidal (SP) toward trigonal bipyramidal (TBP) (Uekusa *et al.*, 1992). The distorted TBP