4,4′-(Ethane-1,2-diyl)dipyridinium di-μ-citrato-bis[aquacobaltate(II)]

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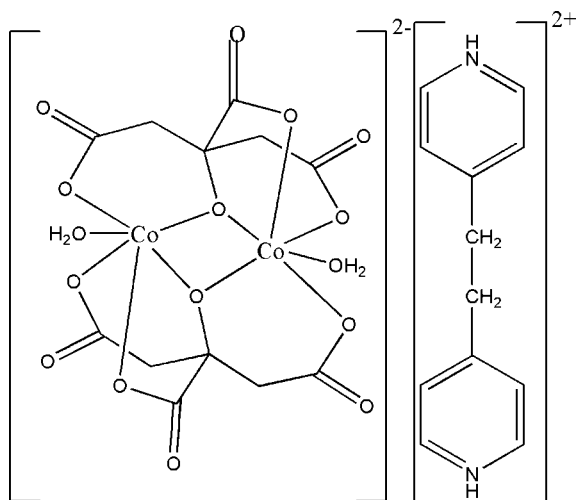
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The anion of the title complex, $(C_{12}H_{14}N_2)[Co_2(C_6H_4O_7)_2(H_2O)_2]$, is a centrosymmetric edge-shared bioctahedral dimer, in which the two Co atoms are bridged by two alkoxide O atoms of the fully deprotonated citrate ligands. All of the carboxylate groups coordinate in a monodentate fashion to terminal positions, and two water molecules complete the slightly distorted octahedral coordination. The dinuclear cation complex and the dianion are organized around inversion centers. Supramolecular O—H···O and N—H···O interactions stabilize the architecture.

Related literature

For related literature, see: Shweky et al. (1994); Srere (1972); Marray (1974).

Experimental

Crystal data

$(C_{12}H_{14}N_2)[Co_2(C_6H_4O_7)_2(H_2O)_2]$	$\gamma = 85.004\ (1)°$
$M_r = 716.33$	$V = 661.72\ (8)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.2975\ (6)$ Å	Mo $K\alpha$ radiation
$b = 9.2340\ (6)$ Å	$\mu = 1.34$ mm^{-1}
$c = 9.9647\ (7)$ Å	$T = 298\ (2)$ K
$\alpha = 65.242\ (1)°$	$0.25 \times 0.20 \times 0.18$ mm
$\beta = 72.803\ (1)°$	

Data collection

Bruker APEXII area-detector diffractometer	5003 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	2437 independent reflections
$T_{min} = 0.730$, $T_{max} = 0.794$	1949 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.118$	
$S = 1.15$	
2437 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.42$ e Å^{-3}
3 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O7	0.86	1.86	2.714 (4)	169
O1W—H1W···O5^i	0.84 (3)	1.773 (17)	2.593 (3)	163 (4)
O1W—H2W···O3^{ii}	0.84 (3)	1.82 (2)	2.608 (3)	154 (4)

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 2, -z + 1$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Bruker, 2004).

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supplementary materials

4,4'-(Ethane-1,2-diyl)dipyridinium di-μ-citrato-bis[aquacobaltate(II)]

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Comment

The prevalent citric acid has been widely known for its abundance in physiological fluids(Srere, 1972). Binuclear iron complexes were studied long ago by the pioneer Marray (Marray, 1974). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metals ions and bridging building blocks as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π-π stacking interactions. In this paper, we report the synthesis and crystal structure of the title complex,(I).

The anionic complex I is an edge-shared bi-octahedral dimer with centro-symmetric structure, in which the two iron atoms are bridged by two alkoxide oxygen atoms of the fully deprotonated citrate ligands. All of the carboxylate groups co-ordinate in a mono-dentate fashion to terminal positions, and two water molecules complete the slightly distorted octahedral coordination spheres. This structure is very similar to those reported by Shweky and coworkers (Shweky *et al.*, 1994). The chelating of the deprotonated hydroxyl and carboxylic groups of the citrate ion leads to two six-membered rings and one five-membered ring, perhaps stabilizing the overall dimeric moiety. Fe—O bond lengths range from 1.9682 (2) −2.0294 (19) Å. Supramolecular interactions (O—H···O and N—H···O) stabilize the architecture(Table 1).

Experimental

citric acid(0.032 g, 0.062 mmol), CoCl2 (0.18 g, 0.21 mmol) and bpa (0.026 g, 0.019 mmol) and NaOH(0.048 mmol,0.12 mmol), were added in a mixed solvent of ethanol and acetonitrile, the mixture was heated for five hours under reflux. during the process stirring and influx were required. The resultant was then filtered to give a pure solution which was infiltrated by diethyl ether freely in a closed vessel, a weeks later some single crystals of the size suitable for X-Ray diffraction analysis.

Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene) and N—H = 0.86 Å with $U_{iso}(H) = 1.2U_{eq}(C$ or N). H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O—H= 0.85 (1)Å and H···H= 1.39 (2) Å) with $U_{iso}(H) = 1.5U_{eq}(O)$.
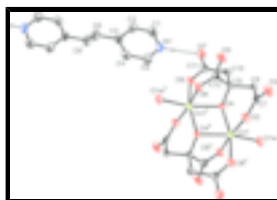
Figures

Fig. 1. Molecular view of (I), showing the atom-labelling scheme·Displacement ellipsoids are shown at the 50% probability level. H atoms not involved in H bonding were omitted for clarity. H bond is represented as dashed line. [Symmetry codes: (i) −x, −y, −z; (ii) 1 − x, −y + 1, −z + 1]

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Triclinic, $P\bar{1}$	$D_x = 1.798$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.2975$ (6) Å	Cell parameters from 2437 reflections
$b = 9.2340$ (6) Å	$\theta = 2.4–25.5°$
$c = 9.9647$ (7) Å	$\mu = 1.34$ mm^{-1}
$\alpha = 65.242$ (1)°	$T = 298$ (2) K
$\beta = 72.803$ (1)°	Block, purple
$\gamma = 85.004$ (1)°	$0.25 \times 0.20 \times 0.18$ mm
$V = 661.72$ (8) Å^3	

Data collection

Bruker APEXII area-detector diffractometer	2437 independent reflections
Radiation source: fine-focus sealed tube	1949 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 298(2)$ K	$\theta_{max} = 25.5°$
φ and ω scans	$\theta_{min} = 2.4°$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -10 \rightarrow 10$
$T_{min} = 0.730$, $T_{max} = 0.794$	$k = -11 \rightarrow 11$
5003 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.3131P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} = 0.001$
2437 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.42$ e Å^{-3}
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1731 (5)	0.4450 (5)	−0.1202 (5)	0.0362 (9)
H1	0.1984	0.5364	−0.2121	0.043*
C2	0.0838 (5)	0.3211 (5)	−0.1064 (5)	0.0362 (9)
H2	0.0476	0.3280	−0.1887	0.043*
C3	0.0457 (5)	0.1833 (4)	0.0304 (5)	0.0301 (9)
C4	0.1005 (5)	0.1797 (5)	0.1488 (5)	0.0387 (10)
H4	0.0756	0.0902	0.2423	0.046*
C5	0.1921 (6)	0.3075 (5)	0.1301 (5)	0.0424 (10)
H5	0.2307	0.3037	0.2101	0.051*
C6	−0.0508 (5)	0.0426 (5)	0.0481 (5)	0.0408 (10)
H6A	−0.1532	0.0790	0.0181	0.049*
H6B	−0.0834	−0.0321	0.1558	0.049*
C7	0.3768 (4)	0.8568 (4)	0.5276 (4)	0.0250 (8)
C8	0.4315 (5)	0.8961 (4)	0.3551 (4)	0.0249 (8)
H8A	0.5501	0.9299	0.3119	0.030*
H8B	0.3672	0.9835	0.3034	0.030*
C9	0.4036 (4)	0.7508 (4)	0.3268 (4)	0.0223 (7)
C10	0.4320 (5)	0.7938 (4)	0.1559 (4)	0.0266 (8)
H10A	0.3629	0.8829	0.1161	0.032*
H10B	0.5492	0.8290	0.1014	0.032*
C11	0.3911 (4)	0.6584 (4)	0.1209 (4)	0.0270 (8)
C12	0.2187 (4)	0.6843 (4)	0.4158 (4)	0.0263 (8)
Co1	0.59943 (6)	0.58334 (5)	0.56194 (6)	0.02524 (19)
N1	0.2251 (4)	0.4365 (4)	−0.0025 (4)	0.0354 (8)
H1A	0.2812	0.5164	−0.0128	0.043*
O2	0.4294 (3)	0.7270 (3)	0.6167 (3)	0.0266 (6)
O3	0.2835 (3)	0.9445 (3)	0.5786 (3)	0.0369 (7)
O4	0.5154 (3)	0.6288 (2)	0.3798 (3)	0.0197 (5)
O5	0.1040 (3)	0.7783 (3)	0.3903 (4)	0.0434 (8)
O6	0.1985 (3)	0.5377 (3)	0.5056 (3)	0.0258 (6)
O7	0.3682 (4)	0.6921 (3)	−0.0064 (3)	0.0396 (7)
O8	0.3806 (3)	0.5148 (3)	0.2227 (3)	0.0310 (6)
O1W	0.7770 (3)	0.7550 (3)	0.4890 (4)	0.0345 (7)

H1W	0.8825 (16)	0.746 (5)	0.474 (5)	0.052*
H2W	0.751 (5)	0.842 (3)	0.497 (5)	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.036 (2)	0.029 (2)	0.036 (2)	0.0009 (17)	−0.0031 (18)	−0.0102 (18)
C2	0.035 (2)	0.041 (2)	0.039 (2)	−0.0038 (18)	−0.0100 (19)	−0.021 (2)
C3	0.0242 (19)	0.026 (2)	0.040 (2)	−0.0006 (15)	−0.0032 (17)	−0.0178 (18)
C4	0.044 (2)	0.028 (2)	0.040 (2)	−0.0026 (18)	−0.013 (2)	−0.0076 (19)
C5	0.048 (3)	0.038 (2)	0.049 (3)	−0.001 (2)	−0.019 (2)	−0.023 (2)
C6	0.032 (2)	0.037 (2)	0.055 (3)	−0.0074 (18)	−0.005 (2)	−0.023 (2)
C7	0.0204 (18)	0.0183 (18)	0.039 (2)	−0.0032 (14)	−0.0100 (16)	−0.0130 (16)
C8	0.0284 (19)	0.0135 (17)	0.036 (2)	0.0015 (14)	−0.0163 (16)	−0.0085 (16)
C9	0.0240 (18)	0.0166 (17)	0.0276 (19)	0.0044 (14)	−0.0131 (15)	−0.0073 (15)
C10	0.0290 (19)	0.0185 (18)	0.031 (2)	0.0011 (15)	−0.0143 (16)	−0.0046 (16)
C11	0.0259 (19)	0.024 (2)	0.033 (2)	0.0018 (15)	−0.0118 (16)	−0.0113 (17)
C12	0.0257 (19)	0.025 (2)	0.032 (2)	−0.0001 (15)	−0.0097 (16)	−0.0141 (17)
Co1	0.0252 (3)	0.0191 (3)	0.0329 (3)	0.00227 (19)	−0.0123 (2)	−0.0098 (2)
N1	0.0302 (18)	0.0284 (18)	0.052 (2)	−0.0042 (14)	−0.0089 (16)	−0.0214 (17)
O2	0.0298 (14)	0.0190 (13)	0.0310 (14)	0.0063 (10)	−0.0096 (11)	−0.0109 (11)
O3	0.0383 (16)	0.0238 (14)	0.0491 (18)	0.0085 (12)	−0.0081 (13)	−0.0199 (13)
O4	0.0202 (12)	0.0143 (11)	0.0268 (13)	0.0037 (9)	−0.0114 (10)	−0.0080 (10)
O5	0.0209 (14)	0.0209 (14)	0.075 (2)	0.0064 (11)	−0.0141 (14)	−0.0082 (14)
O6	0.0220 (13)	0.0151 (12)	0.0352 (15)	−0.0006 (10)	−0.0063 (11)	−0.0067 (11)
O7	0.063 (2)	0.0270 (15)	0.0338 (16)	−0.0007 (13)	−0.0263 (15)	−0.0089 (13)
O8	0.0460 (16)	0.0192 (13)	0.0326 (15)	0.0016 (11)	−0.0199 (13)	−0.0094 (12)
O1W	0.0210 (13)	0.0172 (13)	0.0636 (19)	0.0006 (10)	−0.0119 (14)	−0.0152 (13)

Geometric parameters (Å, °)

C1—N1	1.336 (5)	C9—O4	1.421 (4)
C1—C2	1.354 (5)	C9—C10	1.525 (5)
C1—H1	0.9300	C9—C12	1.556 (5)
C2—C3	1.392 (5)	C10—C11	1.519 (5)
C2—H2	0.9300	C10—H10A	0.9700
C3—C4	1.372 (6)	C10—H10B	0.9700
C3—C6	1.505 (5)	C11—O7	1.243 (4)
C4—C5	1.376 (5)	C11—O8	1.279 (4)
C4—H4	0.9300	C12—O5	1.240 (4)
C5—N1	1.328 (5)	C12—O6	1.264 (4)
C5—H5	0.9300	Co1—O2	1.968 (2)
C6—C6^{i}	1.512 (8)	Co1—O8^{ii}	2.002 (2)
C6—H6A	0.9700	Co1—O4	2.004 (2)
C6—H6B	0.9700	Co1—O1W	2.005 (2)
C7—O3	1.231 (4)	Co1—O4^{ii}	2.031 (2)
C7—O2	1.289 (4)	Co1—O6^{ii}	2.037 (2)
C7—C8	1.529 (5)	N1—H1A	0.8600

C8—C9	1.530 (4)	O1W—H1W	0.84 (3)
C8—H8A	0.9700	O1W—H2W	0.84 (3)
C8—H8B	0.9700		
N1—C1—C2	120.3 (4)	C9—C10—H10A	108.6
N1—C1—H1	119.9	C11—C10—H10B	108.6
C2—C1—H1	119.9	C9—C10—H10B	108.6
C1—C2—C3	120.4 (4)	H10A—C10—H10B	107.6
C1—C2—H2	119.8	O7—C11—O8	122.4 (3)
C3—C2—H2	119.8	O7—C11—C10	118.3 (3)
C4—C3—C2	117.5 (3)	O8—C11—C10	119.4 (3)
C4—C3—C6	120.9 (4)	O5—C12—O6	125.6 (3)
C2—C3—C6	121.5 (4)	O5—C12—C9	117.5 (3)
C3—C4—C5	120.4 (4)	O6—C12—C9	116.9 (3)
C3—C4—H4	119.8	O2—Co1—O8^{ii}	90.26 (10)
C5—C4—H4	119.8	O2—Co1—O4	87.83 (9)
N1—C5—C4	119.8 (4)	O8^{ii}—Co1—O4	161.06 (10)
N1—C5—H5	120.1	O2—Co1—O1W	88.52 (10)
C4—C5—H5	120.1	O8^{ii}—Co1—O1W	93.52 (11)
C3—C6—C6^{i}	112.5 (4)	O4—Co1—O1W	105.27 (11)
C3—C6—H6A	109.1	O2—Co1—O4^{ii}	109.39 (10)
C6^{i}—C6—H6A	109.1	O8^{ii}—Co1—O4^{ii}	85.02 (9)
C3—C6—H6B	109.1	O4—Co1—O4^{ii}	77.87 (10)
C6^{i}—C6—H6B	109.1	O1W—Co1—O4^{ii}	162.01 (10)
H6A—C6—H6B	107.8	O2—Co1—O6^{ii}	171.24 (9)
O3—C7—O2	121.8 (3)	O8^{ii}—Co1—O6^{ii}	90.27 (10)
O3—C7—C8	120.9 (3)	O4—Co1—O6^{ii}	94.46 (9)
O2—C7—C8	117.2 (3)	O1W—Co1—O6^{ii}	82.72 (10)
C7—C8—C9	110.9 (3)	O4^{ii}—Co1—O6^{ii}	79.36 (9)
C7—C8—H8A	109.5	C5—N1—C1	121.5 (3)
C9—C8—H8A	109.5	C5—N1—H1A	119.2
C7—C8—H8B	109.5	C1—N1—H1A	119.2
C9—C8—H8B	109.5	C7—O2—Co1	129.2 (2)
H8A—C8—H8B	108.0	C9—O4—Co1	125.0 (2)
O4—C9—C10	107.7 (3)	C9—O4—Co1^{ii}	107.50 (18)
O4—C9—C8	111.2 (3)	Co1—O4—Co1^{ii}	102.13 (10)
C10—C9—C8	111.7 (3)	C12—O6—Co1^{ii}	110.2 (2)
O4—C9—C12	108.8 (3)	C11—O8—Co1^{ii}	133.7 (2)
C10—C9—C12	108.7 (3)	Co1—O1W—H1W	128 (3)
C8—C9—C12	108.7 (3)	Co1—O1W—H2W	121 (3)
C11—C10—C9	114.5 (3)	H1W—O1W—H2W	109 (5)
C11—C10—H10A	108.6		

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1A$\cdots$O7	0.86	1.86	2.714 (4)	169
O1W—H1W$\cdots$O5^{iii}	0.84 (3)	1.773 (17)	2.593 (3)	163 (4)
O1W—H2W$\cdots$O3^{iv}	0.84 (3)	1.82 (2)	2.608 (3)	154 (4)

Symmetry codes: (iii) $x+1, y, z$; (iv) $-x+1, -y+2, -z+1$.

Fig. 1