

Dipotassium disodium *trans*-bis(pyrazine-2,3-dicarboxylato)copper(II) dithiocyanate dihydrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

H-atom completeness 51%

R factor = 0.040

w R factor = 0.106

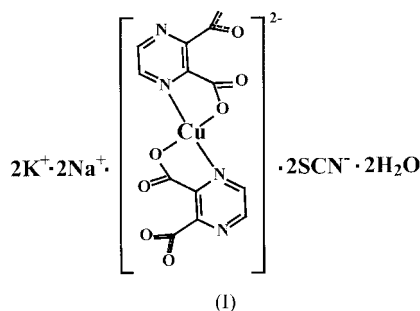
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Reaction of pyrazine-2,3-dicarboxylic acid, NaOH, KSCN and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ led to the formation of $\text{Na}_2\text{K}_2[\text{trans-Cu}(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_2](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$, in which the Cu^{II} atom, on an inversion centre, is approximately in a square-planar environment. This is a new coordination geometry for copper in complexes of pyrazine-2,3-dicarboxylate.

Comment

Takusagawa & Shimada (1973) first determined the structure of pyrazine-2,3-dicarboxylic acid by single-crystal X-ray analysis. Almost at the same time, the first metal-organic compound of pyrazine-2,3-dicarboxylic acid was reported (Richard *et al.*, 1973). More recently, owing to the interest in supramolecular chemistry, pyrazine-2,3-dicarboxylic acid has been intensely investigated (Smith *et al.*, 1995; Neels *et al.*, 1997; Kondo *et al.*, 1999). For further investigation of pyrazine-2,3-dicarboxylic acid, we synthesized the title compound, (I), with a new coordination mode for copper in such complexes. An interesting phenomenon was noted during the synthesis; a blue solid precipitated when pyrazine-2,3-dicarboxylate was added to $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water, but no product was deposited in the presence of SCN^- . Here we report the synthesis and crystal structure of the title compound.



Compound (I) is composed of K^+ and Na^+ cations, $[\text{trans-Cu}(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)_2]^{2-}$ and SCN^- anions, and water molecules. As shown in Fig. 1, the Cu^{II} atom has centrosymmetric square-planar coordination with *trans*-positioned O- and N-donor atoms of two pyrazine-2,3-dicarboxylate ligands. The bond distances $\text{Cu1}-\text{O3}$ and $\text{Cu1}-\text{N3}$ are 1.971 (3) and 1.970 (3) Å, respectively, almost equal to each other, unlike those found in other Cu^{II} complexes of pyrazine-2,3-dicarboxylate (Smith *et al.*, 1995; Neels *et al.*, 1997; Kondo *et al.*, 1999). As in the structures of $\text{C}_{14}\text{H}_8\text{CuN}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (Yucang, Maochun, Rong & Qian, 2001) and $(\text{C}_{28}\text{H}_{24}\text{CuGd}_2\text{N}_4\text{O}_{22})_n \cdot 2n\text{H}_2\text{O}$ (Yucang, Maochun, Weiping *et al.*, 2001), the C—O bond distance of the carboxylate group involving the O atom coordinated to copper in the present compound [$\text{C6}-\text{O3} = 1.276$ (4) Å] is a little longer than the other [$\text{C6}-\text{O4} =$

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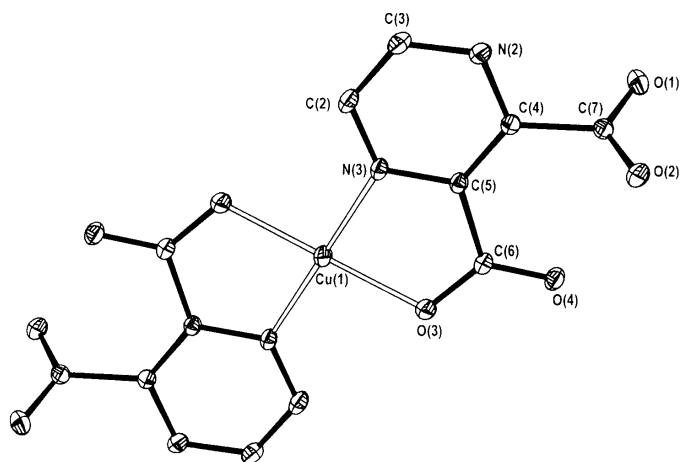


Figure 1
The structure of the $[trans-Cu(C_6H_2N_2O_4)_2]^{2-}$ complex anion, shown with 30% probability ellipsoids. H atoms have been omitted for clarity.

1.237 (4) Å]. However, the two C—O bond distances of the uncoordinated carboxylate group are almost equal, as found in the structure of $(C_{14}H_{22}CuN_2Na_2O_{16})_n$ (Sileo *et al.*, 1999).

As shown in Fig. 2, the three-dimensional framework is constructed through electrostatic interactions among $[trans-Cu(C_6H_2N_2O_4)_2]^{2-}$, SCN^- , K^+ and Na^+ ions, together with water molecules. O—H...N hydrogen bonds are found between O1W and the uncoordinated N atom of pyrazine-2,3-dicarboxylate with a distance of 2.985 (5) Å. Na is six-coordinated by five O atoms and one N atom, while K is eight-coordinated by seven O atoms and one N atom (Table 1).

Experimental

5 ml of a stirred aqueous solution of pyrazine-2,3-dicarboxylic acid (84 mg, 0.5 mmol) was adjusted to pH *ca* 7 with 1 N NaOH aqueous solution, then KSCN (49 mg, 0.5 mmol) was added. After complete dissolution, $Cu(NO_3)_2 \cdot 3H_2O$ (60 mg, 0.25 mmol) was added, giving a clear blue solution, which was filtered. Upon evaporation in air, blue prismatic crystals were obtained in a few days (yield 58%).

Crystal data

$Na_2K_2[Cu(C_6H_2N_2O_4)_2](SCN)_2 \cdot 2H_2O$
 $M_r = 672.10$
 Monoclinic, $P2_1/c$
 $a = 6.8349$ (7) Å
 $b = 6.9692$ (7) Å
 $c = 23.184$ (2) Å
 $\beta = 90.797$ (2)°
 $V = 1104.23$ (19) Å³
 $Z = 2$

$D_x = 2.021$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2150 reflections
 $\theta = 1.8$ – 25.0°
 $\mu = 1.66$ mm⁻¹
 $T = 293$ (2) K
 Prism, blue
 $0.68 \times 0.22 \times 0.18$ mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.514$, $T_{max} = 0.741$
 3306 measured reflections

1929 independent reflections
 1663 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$
 $\theta_{max} = 25.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -6 \rightarrow 8$
 $l = -27 \rightarrow 9$

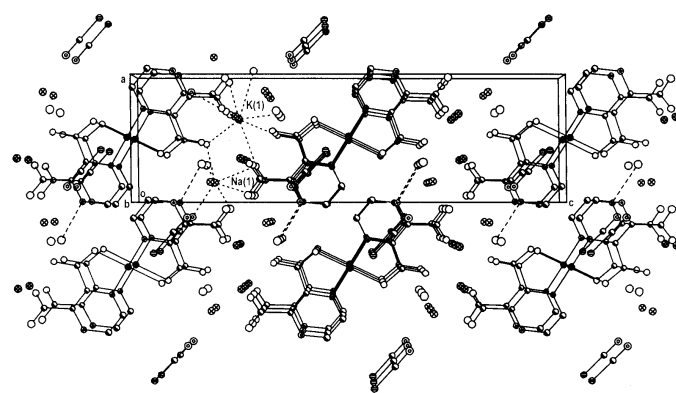


Figure 2
The crystal structure of the title compound, viewed along the *b* axis. H atoms have been omitted and the coordination environments of only one Na ion and one K ion are shown (dotted lines). Dashed lines represent hydrogen bonds.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.106$
 $S = 1.00$
 1929 reflections
 169 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 3.7091P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.50$ e Å⁻³
 $\Delta\rho_{min} = -0.64$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N3	1.970 (3)	Na1—N1	2.370 (4)
Cu1—O3	1.971 (3)	Na1—O2 ⁱ	2.413 (3)
K1—O4 ⁱ	2.776 (3)	Na1—O1W	2.445 (4)
K1—O2 ⁱ	2.820 (3)	Na1—O4	2.465 (3)
K1—O4	2.882 (3)	Na1—O1 ^{vi}	2.596 (4)
K1—O1 ⁱⁱ	2.906 (3)	Na1—O1 ⁱ	2.710 (3)
K1—O1W ⁱⁱⁱ	2.912 (4)	C6—O4	1.237 (4)
K1—O2 ^{iv}	2.928 (3)	C6—O3	1.276 (4)
K1—N1 ^v	3.018 (4)	C7—O2	1.248 (5)
K1—O1	3.239 (3)	C7—O1	1.256 (5)
N3—Cu1—O3	82.42 (11)	O2—C7—O1	126.8 (3)
O4—C6—O3	125.0 (3)	O2—C7—C4	118.4 (3)
O4—C6—C5	120.4 (3)	C6—O3—Cu1	114.0 (2)

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

H atoms were positioned geometrically and refined as riding on their parent atoms; no H atoms were included for the water molecules.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: SAINT and SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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