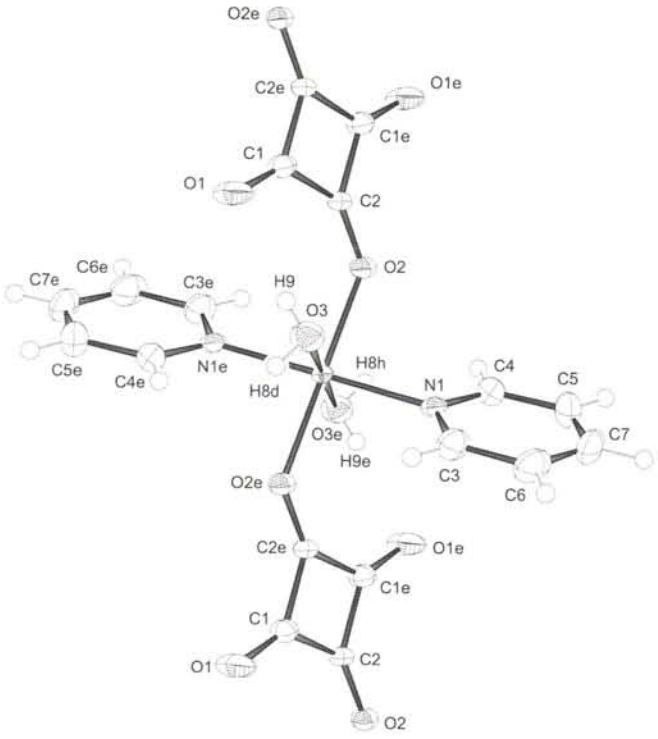
Crystal structure of polymeric diaquabis(pyridine)-μ_2-squarato(1,3)-copper(II), $[Cu(C_4O_4)(C_5H_5N)_2(H_2O)_2]$

E. Krupicka*, A. Grünert and A. Lentz

University of Ulm, Department of Inorganic Chemistry I, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

Received March 27, 2000, CCDC-No. 1267/427



Abstract

$C_{14}H_{14}CuN_2O_6$, orthorhombic, *Pbca* (No. 61), $a = 7.8307(7)$ Å, $b = 12.390(1)$ Å, $c = 15.482(2)$ Å, $V = 1502.1$ Å^3, $Z = 4$, $\rho_m = 1.590$ g·cm^{-3}, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.092$, $T = 293$ K.

Source of material

Single crystals suitable for X-ray analysis have been obtained by mixing 10 ml of 0.1 m copper nitrate solution with 10ml sodium metasilicate solution (1.06 g/ml, pH 5.0). After 48 h the gelling process is finished and a solution, containing 0.1 m sodium-squarate and 0.1 m pyridine, was placed over the set gel. Well developed dark green rod-like crystals are formed within 48 h on the gel-solution interface.

Discussion

Squaric acid (3,4-dihydroxy-cyclobutene-1,2-dione) is known for building a wide variety of complexes with transition metal compounds. Unlike the oxalate ion, the squarate dianion $C_4O_4^{2-}$ does not act as a chelate ligand but as a monodentate bridging ligand, leading to one-dimensional chains or two-dimensional nets. Despite of the structural and magnetic interests, only few crystal structures containing copper(II)squarate and geometrically demanding N-donor-ligands have been investigated [1-4].

In this work we present the crystal strucure of the complex $[Cu(C_5H_5N)_2(H_2O)_2(C_4O_4)]$. The one-dimensional copper(II)-squarate chains are oriented parallel to the *a*-axis and are formed by trans-squarato bridged copper(II)ions. Every copper ion is coordinated by two molecules of pyridine ($d_{Cu1—N1} = 2.01$ Å) and water ($d_{Cu1—O3} = 2.01$ Å) as well as by two oxygen atoms of two different squarate anions ($d_{Cu1—O2} = 2.02$ Å), forming a distorted octahedron. Two types of different hydrogen bonding, formed by the coordinated water molecule (O3) with the noncoordinating oxygen atoms O1 of the squarate anion, can be distinguished: one type is located within every chain (O3-H9-O1) and the other one is connecting two parallel strands of the network (O3-H8-O1). During structure refinement, H atoms bound to the coordinated water molecule O3, were located directly from the difference Fourier synthesis. The remaining H atomes (pyridine) were geometrically set as idealized aromatic C-H groups using a riding model.

Table 1. Data collection and handling.

Crystal:	green block, size 0.15 × 0.39 × 0.46 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.87 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2.0°$
$2\theta_{max}$:	51.88°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1453, 1453
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 991
$N(param)_{refined}$:	114
Programs:	SHELXS-97 [5], SHELXL-97 [6], PLATON92 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5)	8*c*	0.0596	–0.2678	0.2645	0.049
H(4)	8*c*	–0.0039	–0.2049	0.4007	0.035
H(3)	8*c*	0.1577	0.0834	0.3396	0.037
H(6)	8*c*	0.2274	0.0265	0.2027	0.050
H(7)	8*c*	0.1740	–0.1504	0.1631	0.052
H(8)	8*c*	–0.536(6)	0.286(4)	0.560(3)	0.07(2)
H(9)	8*c*	–0.168(6)	0.171(3)	0.451(3)	0.04(1)

* Correspondence author (e-mail: erik.krupicka@chemie-uni-ulm.de)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*b*	0	0	1/2	0.0099(2)	0.0236(3)	0.0154(2)	–0.0006(2)	0.0008(2)	–0.0027(2)
O(1)	8*c*	–0.3935(3)	0.1694(2)	0.5206(2)	0.016(1)	0.021(1)	0.070(2)	–0.0013(9)	0.002(1)	–0.0061(9)
O(2)	8*c*	–0.2316(3)	–0.0701(1)	0.4841(1)	0.014(1)	0.0226(9)	0.028(1)	0.0017(8)	–0.0007(8)	–0.0037(8)
N(1)	8*c*	0.0677(3)	–0.0549(2)	0.3828(1)	0.012(1)	0.032(1)	0.019(1)	0.001(1)	0.0009(9)	–0.001(1)
C(1)	8*c*	–0.4519(4)	0.0770(2)	0.5097(2)	0.016(1)	0.020(1)	0.029(2)	0.001(1)	0.000(1)	–0.001(1)
C(5)	8*c*	0.0799(5)	–0.1960(3)	0.2786(2)	0.039(2)	0.047(2)	0.038(2)	0.005(2)	–0.003(2)	–0.020(2)
C(2)	8*c*	–0.3778(4)	–0.0302(2)	0.4930(2)	0.011(1)	0.020(1)	0.021(1)	0.000(1)	–0.000(1)	–0.001(1)
C(4)	8*c*	0.0416(4)	–0.1576(2)	0.3602(2)	0.025(2)	0.035(2)	0.027(2)	0.001(1)	–0.001(1)	–0.005(1)
C(3)	8*c*	0.1372(4)	0.0120(2)	0.3242(2)	0.030(2)	0.038(2)	0.026(2)	–0.002(2)	0.004(1)	0.003(1)
C(6)	8*c*	0.1791(5)	–0.0215(3)	0.2419(2)	0.033(2)	0.067(2)	0.026(2)	0.000(2)	0.008(1)	0.005(2)
C(7)	8*c*	0.1487(5)	–0.1265(3)	0.2186(2)	0.035(2)	0.073(3)	0.022(2)	0.009(2)	0.003(2)	–0.013(2)
O(3)	8*c*	–0.0946(4)	0.1605(2)	0.4302(2)	0.026(1)	0.026(1)	0.042(1)	–0.003(1)	0.002(1)	–0.003(1)

Acknowledgment. One of us (EK) would like to thank the Landesgraduiertenförderungsprogramm (LGFP) for financial support.

References

1. Solans, X.; Aguilo, M.; Gleizes, A.: Coordination Modes of the Squarate Ligand: Synthesis and Crystal Structure of Six Copper(II)Squarate Complexes. Inorg. Chem. **29** (1990) 775-784.
2. Graf, M.; Stoeckli-Evans, H.; Escuer, A.: Significant antiferromagnetic exchange in copper(II) and nickel(II) dinuclear complexes of the substituted pyrazine ligand 2,3,5,6-tetra(2-pyridyl)pyrazin (TPPZ): magnetic properties, synthesis and crystal structure. Inorg. Chim. Acta. **257** (1997) 89-97.
3. Yaghi, O. M.; Li, G.; Groy, T. L.: Preparation of Single Crystals of Coordination Solids in Silica Gels: Synthesis and Crystal Structure of Cu(II)(1,4-$C_4H_4N_2$)(C_4O_4)(H_2O)$_4$. J. Solid State Chem. **117** (1995) 256-260.
4. Bernardinelli, G.; Deguenon, D.; Soules, R.: Versatility of squaric acid as ligand. Crystal, molecular structures and magnetic studies of four poly-od dimetallic Cu(II)complexes. Can. J. Chem. **67** (1989) 1158-1165.
5. Sheldrick, G. M.: SHELXS-97. Program for the Solution of crystal structures. University of Göttingen, Germany 1997.
6. Sheldrick, G. M.: SHELX-L97. Program for the Refinement of crystal structures. University of Göttingen, Germany 1997.
7. Spek, A. L.: PLATON92. Molecular Geometry Program. University of Utrecht, The Netherlands 1992.