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The crystal structure of 2,6-bis(pyridin-1-ium-3-ylmethyl)hexahydro-4,8-ethenopyrrolo-[3,4-*f*] isoindole-1,3,5,7-tetrone tetrachloridocuprate(II) monohydrate, $C_{24}H_{24}Cl_4CuN_4O_5$

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.20 × 0.20 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.29 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	27.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16290, 5688, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 4783
$N(\text{param})_{\text{refined}}$:	349
Programs:	Bruker programs [1], SHELX [2, 3]

<https://doi.org/10.1515/ncrs-2019-0102>

Received February 3, 2019; accepted March 19, 2019; available online April 8, 2019

Abstract

$C_{24}H_{24}Cl_4CuN_4O_5$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 11.8748(12)$ Å, $b = 13.3493(13)$ Å, $c = 16.4721(17)$ Å, $V = 2611.2(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0351$, $wR_{\text{ref}}(F^2) = 0.0873$, $T = 173(2)$ K.

CCDC no.: 1435893

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

In a representative experiment 5 mL $CHCl_3$ solution of 2,6-bis(pyridin-3-ylmethyl)hexahydro-4,8-ethenopyrrolo-[3,4-*f*] isoindole-1,3,5,7-tetrone (1 mmol, 0.43 g) was added to one leg of an H-shaped tube, and a 6 mL mix solution of $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.34 g) in ethanol/(0.01 M)HCl(v:v = 1:1) was added to the other leg of the tube. The prism yellow single crystals were obtained after ten days.

Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(H)$ set to $1.2U_{\text{eq}}(C)$. The H atoms of the water molecule were located on a difference Fourier map and refined with $U_{\text{iso}}(H)$ set to $1.5U_{\text{eq}}(O)$. The N-bound H atoms were located on a difference Fourier map but were later refined as riding, with $U_{\text{iso}}(H)$ set to $1.2U_{\text{eq}}(N)$. It should be mentioned that the highest difference density peak (0.83 eÅ^{-3}) is located 1.744 Å away from C13 and could not be assigned to any chemically meaningful disordered atom. The next highest residual density peaks are in the range $0.37\text{--}0.50 \text{ eÅ}^{-3}$ and are all located around the copper tetrachloride anion.

Comment

The ligand 2,6-bis(pyridin-3-ylmethyl)hexahydro-4,8-ethenopyrrolo-[3,4-*f*]isoindole-1,3,5,7-tetrone has two terminal pyridine groups that can adopt different conformations with respect to the methylene bridge and exhibits a variety of architectures [4, 5]. The work reported in this paper is a continuation of our previous studies on isoindole dione containing complexes [6, 7], including work on neutral and monoprotonated ligands [8, 9]. Many complexes containing the $(CuCl_4)^{2-}$ anion have been studied for their thermochroism and phase transitions [10, 11].

In this paper, we report the new crystal structure of $(C_{24}H_{22}N_4O_4)^{2+} \cdot (CuCl_4)^{2-} \cdot H_2O$. The unit cell of the title salt contains one tetrachloridocuprate(II) anion, one organic diprotonated cation and one water molecule (*cf.* the figure). In the anion the Cu^{II} metal atom exhibits a typical tetrahedral

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.09002(4)	0.66745(4)	0.78972(3)	0.02377(14)
Cl1	0.22611(10)	0.55303(10)	0.80628(8)	0.0385(3)
Cl2	0.07069(11)	0.77297(9)	0.68557(7)	0.0386(3)
Cl3	−0.06469(9)	0.57268(9)	0.77803(7)	0.0322(3)
Cl4	0.14015(10)	0.76960(9)	0.89115(6)	0.0285(2)
O1	0.6744(3)	0.5580(3)	0.5997(2)	0.0335(8)
O2	0.4967(3)	0.2575(3)	0.6163(2)	0.0380(8)
O3	0.6939(3)	0.5795(3)	0.95887(19)	0.0334(8)
O4	0.4871(3)	0.2931(3)	0.9683(2)	0.0375(9)
N1	0.3439(4)	0.6383(3)	0.4442(2)	0.0351(10)
H2A	0.335860	0.674633	0.401491	0.042*
N2	0.5790(3)	0.4100(3)	0.5910(2)	0.0249(8)
N3	0.5805(3)	0.4436(3)	0.9801(2)	0.0239(8)
N4	0.3098(3)	0.6469(3)	0.9948(2)	0.0308(9)
H22A	0.276464	0.663930	0.950523	0.037*
C1	0.2743(4)	0.6524(4)	0.5058(3)	0.0348(12)
H1B	0.217586	0.700206	0.502177	0.042*
C2	0.2861(4)	0.5966(4)	0.5745(3)	0.0345(12)
H1A	0.238308	0.606488	0.618481	0.041*
C3	0.3705(4)	0.5250(4)	0.5779(3)	0.0312(11)
H5A	0.379524	0.486763	0.624674	0.037*
C4	0.4415(4)	0.5098(3)	0.5122(3)	0.0250(10)
C5	0.4264(4)	0.5698(3)	0.4453(3)	0.0318(11)
H3A	0.473697	0.562843	0.400658	0.038*
C6	0.5301(4)	0.4285(4)	0.5108(3)	0.0298(11)
H6A	0.496555	0.367065	0.490774	0.036*
H6B	0.589524	0.447686	0.473498	0.036*
C7	0.6490(4)	0.4777(4)	0.6295(3)	0.0257(10)
C8	0.6837(3)	0.4361(3)	0.7104(3)	0.0227(9)
H8A	0.765377	0.426004	0.711737	0.027*
C9	0.6226(3)	0.3339(3)	0.7159(3)	0.0243(9)
H9A	0.677960	0.279732	0.719993	0.029*
C10	0.5573(4)	0.3246(4)	0.6368(3)	0.0253(10)
C11	0.5443(3)	0.3322(3)	0.7902(3)	0.0241(9)
H11A	0.501811	0.269339	0.793381	0.029*
C12	0.4673(4)	0.4212(3)	0.7862(3)	0.0249(9)
H12A	0.389242	0.415475	0.785731	0.030*
C13	0.5208(4)	0.5102(4)	0.7832(3)	0.0251(9)
H13A	0.482729	0.571072	0.781956	0.030*
C14	0.6472(4)	0.5027(3)	0.7820(3)	0.0217(9)
H14A	0.682187	0.569082	0.778990	0.026*
C15	0.6858(3)	0.4455(3)	0.8584(2)	0.0195(9)
H15A	0.766973	0.432772	0.855557	0.023*
C16	0.6576(4)	0.5002(3)	0.9373(3)	0.0229(9)
C17	0.5539(4)	0.3534(3)	0.9423(3)	0.0261(10)
C18	0.6217(4)	0.3457(3)	0.8642(3)	0.0241(10)
H18A	0.674996	0.289879	0.867677	0.029*
C19	0.5396(4)	0.4716(4)	1.0605(3)	0.0266(10)
H19A	0.602304	0.497601	1.091873	0.032*
H19B	0.512617	0.411822	1.087786	0.032*
C20	0.4464(3)	0.5487(3)	1.0604(3)	0.0231(9)
C21	0.4144(4)	0.5925(3)	1.1332(3)	0.0299(10)
H24A	0.450294	0.574009	1.181060	0.036*
C22	0.3291(4)	0.6636(4)	1.1351(3)	0.0365(12)
H4A	0.307128	0.692702	1.183936	0.044*
C23	0.2775(4)	0.6904(4)	1.0628(3)	0.0347(12)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H23A	0.220722	0.738351	1.062313	0.042*
C24	0.3917(4)	0.5777(4)	0.9905(3)	0.0274(10)
H21A	0.411240	0.549591	0.940766	0.033*
O1W	0.2851(3)	0.7751(3)	0.3308(2)	0.0403(9)
H1C	0.337(4)	0.802(4)	0.307(4)	0.060*
H1D	0.246(4)	0.817(3)	0.353(3)	0.060*

environment, with Cu–Cl distances ranging from 2.2316(9) to 2.2403(9) Å, and with Cl–Cu–Cl angles ranging from 97.63(4) to 128.82(4)°. The backbone of the cation is U-shaped, with the two isoindole dione rings (N2/C7–C10 and N3/C15–C18) inclined to one another by 53.612(96)°, while the two outer pyridinium rings (N1/C1–C5 and N4/C20–C24) are inclined to one another by 30.107(103)°. The dihedral angles between the pyridinium ring and the adjacent isoindole dione ring are 88.003(104)° for rings N1/C1–C5 and N2/C7–C10, and 83.086(118)° for rings N4/C20–C24 and N3/C15–C18. The bond angles C4–C6–N2 and C20–C19–N3 are 112.6(3) and 114.6(3)°. In the crystal, O–H···Cl, O–H···O, N–H···O and N–H···Cl hydrogen bonds link the cations, anions and solvent water molecules into a three-dimensional network.

Acknowledgements: We gratefully acknowledge financial support from the Doctoral Research Fund of Shanxi University (No. 112536901013).

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