Crystal structure of bis(μ-6-olato-2,2'-bipyridine-$\kappa^3N,N':O$)-dicopper(I) —pentafluorotantalum(V) (1:1), $[Cu_2(C_{10}H_7N_2O)_2][TaF_5]$, $C_{20}H_{14}Cu_2F_5N_4O_2Ta$

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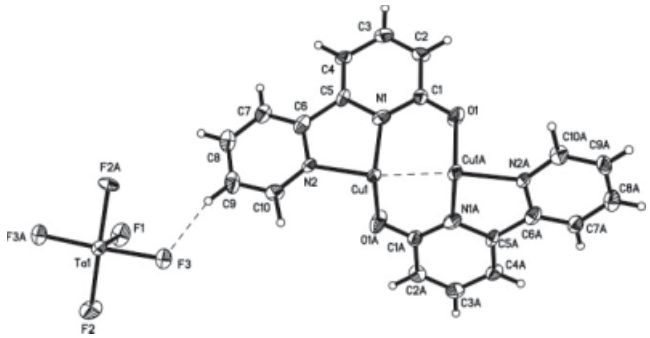

Abstract

$C_{20}H_{14}Cu_2F_5N_4O_2Ta$, monoclinic, *C*2 (no. 5), a = 18.372(9) Å, b = 3.860(2) Å, c = 16.038(8) Å, β = 115.086(7)°, V = 1029.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.0407, $wR_{ref}(F^2)$ = 0.1083, T = 296 K.

Table 1. Data collection and handling.

Crystal:	black blocks, size 0.12×0.15×0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	74.18 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	51.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2644, 1830
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1697
$N(param)_{refined}$:	156
Programs:	SHELX [11]

Source of material

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The mixture of 0.22 g Ta_2O_5, 0.44 g HF (40 *wt*%), 0.80 g CuO, 0.22 g 2,2'-bipyridine, 0.22 g 2,6-diaminopyridine and 10 ml H_2O was stirred for half an hour, and transferred into a Teflon-lined stainless steel autoclave (50 ml) and treated at 443 K for 8 days. After the mixture was slowly cooled to room temperature, black block shaped crystals suitable for X-ray structure determination were obtained. In order to confirm the chemical composition, C, H, and N elemental analysis were performed on a PerkinElmer 2400II elemental analyzer. Anal. calcd.: C, 32.23; H, 1.89; N, 7.52%. Found: C, 32.61; H, 1.64; N, 7.87%.

Experimental details

The H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å and with U_{iso}(H) = 1.2 U_{eq}(C). The C2, C3, C4, C10 and F1 atoms were refined with restraint (isor 0.01) due to their slight disorders. In addition, the C1, C2, C3, C4, C5 and N1 atoms were refined with restraint (flat 0.01). The Flack parameter indicates an inversion twin.

Discussion

The tantalum fluorides have received much attention in recently years due to their specific structure-related properties [1-5]. In this article, we report a new tantalum fluoride (Fig.) obtained with the use of 2,2'-bipyridine ligand under hydrothermal conditions. The asymmetric unit of the title structure contains one half of a C_2 symmetric $[Cu^I_2(C_{10}H_7N_2O)_2]$ and one half of a C_2 symmetric TaF_5. Bond valence calculations [6, 7] reveal that the valence of the Cu(1) site is +1. In the structure of $[Cu^I_2(C_{10}H_7N_2O)_2]$, each copper (I) is coordinated by two N atoms and one O atom from two different 6-olato-2,2'-bipyridine ligands. In addition, there are the weak interactions between the copper atoms due to the distance 2.400(2) Å of Cu···Cu. The Ta^V metal center is five-coordinated by five fluorine atoms in the first coordination shell, forming a $\{TaF_5\}$ square-pyramidal coordination geometry. The bond lengths of Ta–F are 1.80(2)-1.912(6) Å. The bond lengths are consistent with those reported for known tantalum fluorides [8-10]. These square-pyramids are further connected to each other via *trans*-fluorine atoms [Ta–F: 2.06(2) Å], forming an infinite linear structure of corner-shared octahedrons. Moreover, the $[Cu_2(C_{10}H_7N_2O)_2]$ and TaF_5 are connected through non-classical C–H···F hydrogen bonds into three-dimensional supramolecular structure: C9–H9···F3 (2.28 Å and 3.18(2) Å, 163°) and C8–H8···F2^v (2.53 Å and 3.288(16) Å, 139°). Symmetry code: -x, y-1, -z.

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*c*	0.6853	0.0082	0.4355	0.053
H(3)	4*c*	0.6297	–0.1350	0.2838	0.073
H(4)	4*c*	0.4921	–0.0042	0.1920	0.050
H(7)	4*c*	0.3586	0.0986	0.1207	0.055
H(8)	4*c*	0.2263	0.2780	0.0549	0.061
H(9)	4*c*	0.1810	0.6623	0.1446	0.072
H(10)	4*c*	0.2585	0.6297	0.2984	0.059

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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}
Ta(1)	2*a*	0	1.058(1)	0	0.0403(3)	0.0270(3)	0.0290(3)	0	0.0164(2)	0
Cu(1)	4*c*	0.44181(6)	0.559(2)	0.42753(7)	0.0373(6)	0.0497(7)	0.0244(6)	0.005(3)	0.0131(5)	–0.012(2)
F(1)	2*a*	0	0.524(6)	0	0.087(6)	0.023(7)	0.058(5)	0	0.022(4)	0
F(2)	4*c*	–0.0859(4)	1.044(5)	0.0360(4)	0.054(4)	0.076(5)	0.063(4)	–0.033(7)	0.037(3)	0.003(8)
F(3)	4*c*	0.0758(4)	1.015(4)	0.1258(4)	0.052(3)	0.021(7)	0.039(3)	0.001(4)	0.011(3)	–0.001(3)
N(1)	4*c*	0.5089(7)	0.289(3)	0.3860(7)	0.059(7)	0.044(6)	0.039(5)	0.003(5)	0.029(5)	–0.006(5)
N(2)	4*c*	0.3573(6)	0.476(3)	0.2968(6)	0.038(5)	0.06(1)	0.022(4)	–0.001(5)	0.014(4)	–0.007(4)
C(1)	4*c*	0.5860(7)	0.219(2)	0.4393(8)	0.038(6)	0.043(6)	0.033(6)	0.004(5)	0.014(5)	0.002(5)
C(2)	4*c*	0.6314(6)	0.058(2)	0.3994(7)	0.041(4)	0.047(5)	0.050(5)	0.009(8)	0.025(4)	–0.024(8)
C(3)	4*c*	0.5988(8)	–0.027(3)	0.3096(9)	0.054(6)	0.09(1)	0.051(6)	–0.001(6)	0.034(5)	–0.011(6)
C(4)	4*c*	0.5159(6)	0.050(4)	0.2543(7)	0.053(5)	0.044(5)	0.037(4)	0.018(8)	0.027(4)	–0.002(8)
C(5)	4*c*	0.4735(7)	0.202(3)	0.2937(7)	0.049(6)	0.032(5)	0.022(5)	–0.008(5)	0.009(5)	–0.001(4)
C(6)	4*c*	0.3872(8)	0.310(4)	0.2428(8)	0.063(8)	0.030(6)	0.034(6)	–0.007(6)	0.018(6)	0.003(5)
C(7)	4*c*	0.3386(8)	0.230(4)	0.1551(8)	0.052(8)	0.044(7)	0.036(6)	–0.016(6)	0.014(6)	–0.002(6)
C(8)	4*c*	0.2598(8)	0.338(4)	0.1153(9)	0.054(8)	0.040(8)	0.045(7)	–0.009(6)	0.007(7)	0.002(6)
C(9)	4*c*	0.2301(7)	0.547(8)	0.1695(8)	0.035(5)	0.08(1)	0.046(6)	–0.03(1)	0.003(5)	0.02(2)
C(10)	4*c*	0.2803(6)	0.557(7)	0.2585(7)	0.053(5)	0.050(5)	0.045(5)	0.006(8)	0.021(4)	–0.026(7)
O(1)	4*c*	0.6160(6)	0.306(4)	0.5235(6)	0.069(6)	0.096(8)	0.033(5)	0.041(6)	0.015(5)	–0.017(5)

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