Crystal structure of aquabis(2,2′-bipyridyl-*N*,*N*′)(9,10-dioxo-anthracene-2,6-disulfonato)copper(II) — water (1:3), $[Cu(H_2O)(C_{10}H_8N_2)_2][C_{14}H_6S_2O_8] \cdot 3H_2O$

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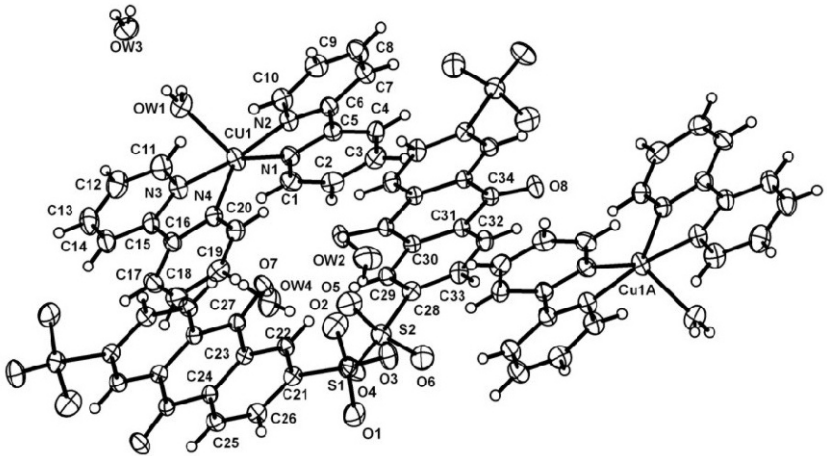

Abstract

$C_{34}H_{30}CuN_4O_{12}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 11.116(4) Å, b = 11.168(7) Å, c = 15.082(4) Å, α = 80.23(4)°, β = 82.57(3)°, γ = 66.33(4)°, V = 1686.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.082, $wR_{ref}(F^2)$ = 0.276, T = 298 K.

Source of material

A mixture of 0.17 g of $CuCl_2 \cdot 2H_2O$ (1 mmol), 0.16 g of 2,2′-bipyridine (1 mmol), 0.31 g of 9,10-dioxoanthracene-2,6-disulfonic acid disodium salt (1 mmol), and 15 mL of deionized water was sealed into a bomb equipped with a Teflon liner (25 mL) and heated at 373 K for 2 days. Blue rod-shaped crystals of the title compound were obtained when the sample was cooled to room temperature (yield 62 % based on Cu).

Elemental analysis — found: C, 50.11 %; H, 3.75 %; N, 6.73 %; calculated for $C_{34}H_{30}CuN_4O_{12}S_2$: C, 50.15 %; H, 3.71 %; N, 6.88 %.

Experimental details

The C-bound H atoms were geometrically placed with d(C—H) = 0.93 Å and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The O-bound H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.2 U_{eq}(O). The high R-value is caused by the quality of the crystal.

Discussion

The use of multifunctional ligands for the construction of coordination polymers by coordinating to metal centers is of current interest. The coordination chemistry of the multidentate N/O-donor ligands containing rigid frameworks, such as polycarboxylates, polybipyridines or their derivatives, and mixed polycarboxylate and polybipyridine ligands has been widely investigated [1-3]. However, the ligand 2,6-ADS (9,10-dioxoanthracene-2,6-disulfonic acid disodium salt) has been little explored. In our previous works, we have reported a transition metal sulfonate based on 2,6-ADS [4].

The asymmetric unit of the title crystal structure is composed of one copper ion, two fragments of 2,6-ADS anions, two 2,2′-bipy ligands, one water ligand, and three lattice water molecules. The Cu(II) ion is coordinated by four nitrogen atoms from two 2,2′-bipy ligands and one oxygen atom from a water ligand. The angles subtended at Cu(II) atom by *cis* pairs of ligating atoms cover the range 80.63(2)° to 171.38(2)°, and the angles subtended by the *trans* pairs are in the range 100.11(2)° to 105.08(2)°, indicative of serious distortion of the $[CuON_4]$ square-planar coordination. The distances d(Cu—N) range from 1.979(4) Å to 2.058(4) Å, which are comparable to d(Cu—O) = 2.169(4) Å reported in other Cu(II) complexes [5]. The angle of the planes through the 2,2′-bipy ligands coordinated to the Cu centre is 57.12(4)°. The 2,6-ADS anion does not participate in the coordination of the Cu(II) atom, and has an inversion centre at the midpoint of the central C—C bond. The average distance d(S—O) = 1.443(4) Å falls within the typical range of d(S—O) in a sulfonate ion, and the average distance d(C—S) = 1.785(4) Å is also as expected for a 2,6-ADS anion. In the compound, the nearest distance of a pyridine ring to the adjacent Cu cation (3.69 Å) suggests an offset face-to-face aromatic interaction, resulting in polymeric cation chains propagating in an infinite chain of [001]. The 2,6-ADS anions interact with each other via O–H···O hydrogen bonds between the sulfonate groups and the lattice water molecules, resulting in the formation of infinte chains. The cation

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chains and anion chains align in a neat alternating mode, which is made possible by the well matched ionic size. These chains are further linked by lattice water molecules via O–H···O hydrogen bonds forming a 3D packing structure.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.28 × 0.33 × 0.40 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	27.08 cm^{-1}
Diffractometer, scan mode:	Xcalibur Nova, Onyx CCD, κ geometry, ω
$2\theta_{max}$:	135°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17183, 6041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5043
$N(param)_{refined}$:	479
Programs:	SHELXS-97, SHELXL-97, SHELXTL [6]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	1.1242	0.0394	0.2328	0.106
H(1B)	2*i*	1.0241	–0.0165	0.2530	0.106
H(2A)	2*i*	0.7546	0.8005	0.3233	0.127
H(2B)	2*i*	0.8906	0.7271	0.3404	0.127
H(3A)	2*i*	1.1902	–0.2756	0.2346	0.107
H(3B)	2*i*	1.2547	–0.1983	0.2618	0.107
H(4A)	2*i*	0.1976	0.2406	0.1778	0.115
H(4B)	2*i*	0.2838	0.1248	0.1376	0.115
H(1)	2*i*	0.5740	0.1255	0.2556	0.080
H(2)	2*i*	0.3986	0.1298	0.3539	0.090
H(3)	2*i*	0.4016	0.1539	0.5030	0.088
H(4)	2*i*	0.5833	0.1690	0.5497	0.077
H(7)	2*i*	0.7828	0.1485	0.5861	0.084
H(8)	2*i*	0.9774	0.1687	0.6074	0.095
H(9)	2*i*	1.1041	0.2140	0.4831	0.096
H(10)	2*i*	1.0439	0.2254	0.3413	0.088
H(11)	2*i*	0.7917	–0.0528	0.1963	0.100
H(12)	2*i*	0.7955	–0.1175	0.0581	0.112
H(13)	2*i*	0.8177	0.0136	–0.0719	0.109
H(14)	2*i*	0.8360	0.2109	–0.0629	0.092
H(17)	2*i*	0.8306	0.4063	–0.0435	0.083
H(18)	2*i*	0.8478	0.5930	–0.0095	0.090
H(19)	2*i*	0.8646	0.6094	0.1400	0.089
H(20)	2*i*	0.8646	0.4401	0.2487	0.078
H(22)	2*i*	0.5082	0.5960	0.2005	0.062
H(25)	2*i*	0.5289	0.7853	–0.0964	0.067
H(26)	2*i*	0.5340	0.8943	0.0202	0.069
H(29)	2*i*	0.4002	0.4836	0.2995	0.063
H(32)	2*i*	0.2141	0.4766	0.5938	0.071
H(33)	2*i*	0.1041	0.4657	0.4768	0.075

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)	2*i*	0.83511(7)	0.16858(7)	0.26132(4)	0.0823(5)	0.0784(5)	0.0482(5)	–0.0466(4)	0.0035(3)	–0.0111(3)
S(1)	2*i*	0.5122(1)	0.8452(1)	0.21145(8)	0.0691(7)	0.0628(6)	0.0647(7)	–0.0312(5)	–0.0048(5)	–0.0216(5)
S(2)	2*i*	0.1479(1)	0.4797(1)	0.28781(8)	0.0629(6)	0.0704(7)	0.0673(7)	–0.0320(5)	–0.0111(5)	–0.0164(5)
O(1)	2*i*	0.4665(4)	0.9821(3)	0.1732(3)	0.111(3)	0.058(2)	0.091(3)	–0.037(2)	0.002(2)	–0.026(2)
O(2)	2*i*	0.6457(4)	0.7949(5)	0.2368(4)	0.081(2)	0.123(3)	0.130(4)	–0.030(2)	–0.038(2)	–0.054(3)
O(3)	2*i*	0.4233(4)	0.8155(4)	0.2810(3)	0.115(3)	0.100(3)	0.068(2)	–0.065(2)	0.015(2)	–0.036(2)
O(5)	2*i*	0.1946(4)	0.3443(4)	0.2720(3)	0.103(3)	0.079(2)	0.110(3)	–0.039(2)	–0.028(2)	–0.030(2)
O(4)	2*i*	0.1781(4)	0.5641(4)	0.2120(3)	0.111(3)	0.105(3)	0.065(2)	–0.061(2)	–0.027(2)	0.002(2)
O(6)	2*i*	0.0114(3)	0.5284(5)	0.3226(3)	0.058(2)	0.127(3)	0.094(3)	–0.036(2)	–0.011(2)	–0.030(2)
O(8)	2*i*	0.3801(3)	0.5242(4)	0.6656(2)	0.063(2)	0.097(2)	0.045(2)	–0.039(2)	0.005(1)	–0.019(1)
O(7)	2*i*	0.5130(4)	0.3791(3)	0.1698(2)	0.107(2)	0.060(2)	0.045(2)	–0.041(2)	–0.004(2)	–0.003(1)
OW(1)	2*i*	1.0433(4)	0.0512(4)	0.2386(3)	0.079(2)	0.080(2)	0.103(3)	–0.027(2)	0.011(2)	–0.026(2)
OW(2)	2*i*	0.8185(5)	0.7897(5)	0.3538(3)	0.115(3)	0.102(3)	0.113(3)	–0.046(3)	–0.043(3)	–0.012(3)
OW(3)	2*i*	1.1918(4)	–0.2005(4)	0.2365(3)	0.089(2)	0.072(2)	0.105(3)	–0.029(2)	–0.005(2)	–0.009(2)
OW(4)	2*i*	0.2062(4)	0.1716(5)	0.1565(3)	0.096(3)	0.101(3)	0.110(3)	–0.050(2)	0.009(2)	–0.047(2)
N(1)	2*i*	0.6847(4)	0.1432(3)	0.3412(2)	0.068(2)	0.061(2)	0.053(2)	–0.032(2)	–0.005(2)	–0.006(2)
N(2)	2*i*	0.8805(4)	0.1936(4)	0.3783(3)	0.072(2)	0.069(2)	0.054(2)	–0.034(2)	0.001(2)	–0.012(2)
N(3)	2*i*	0.8097(4)	0.1161(4)	0.1485(3)	0.080(2)	0.082(2)	0.057(2)	–0.040(2)	0.006(2)	–0.018(2)
N(4)	2*i*	0.8460(3)	0.3255(4)	0.1717(2)	0.055(2)	0.065(2)	0.053(2)	–0.028(2)	0.003(1)	–0.012(1)
C(1)	2*i*	0.5764(5)	0.1341(5)	0.3155(3)	0.079(3)	0.064(2)	0.063(3)	–0.036(2)	–0.011(2)	0.001(2)
C(2)	2*i*	0.4709(5)	0.1370(5)	0.3738(4)	0.071(3)	0.070(3)	0.089(4)	–0.034(2)	–0.007(2)	0.000(2)
C(3)	2*i*	0.4729(5)	0.1508(5)	0.4624(4)	0.070(3)	0.059(2)	0.088(4)	–0.028(2)	0.012(2)	–0.006(2)
C(4)	2*i*	0.5807(5)	0.1601(4)	0.4899(3)	0.077(3)	0.056(2)	0.063(3)	–0.031(2)	0.014(2)	–0.015(2)
C(5)	2*i*	0.6866(4)	0.1562(4)	0.4285(3)	0.073(2)	0.048(2)	0.054(2)	–0.027(2)	0.002(2)	–0.006(2)
C(6)	2*i*	0.8059(4)	0.1713(4)	0.4495(3)	0.072(2)	0.051(2)	0.051(2)	–0.027(2)	–0.001(2)	–0.008(2)
C(7)	2*i*	0.8375(6)	0.1629(5)	0.5371(3)	0.090(3)	0.072(3)	0.053(2)	–0.039(2)	–0.004(2)	–0.008(2)
C(8)	2*i*	0.9522(6)	0.1766(6)	0.5495(4)	0.100(4)	0.087(3)	0.062(3)	–0.045(3)	–0.012(3)	–0.013(2)
C(9)	2*i*	1.0281(6)	0.2019(6)	0.4758(4)	0.082(3)	0.084(3)	0.087(4)	–0.039(3)	–0.017(3)	–0.018(3)
C(10)	2*i*	0.9914(5)	0.2093(5)	0.3912(4)	0.078(3)	0.085(3)	0.069(3)	–0.042(2)	–0.003(2)	–0.015(2)
C(11)	2*i*	0.8002(6)	0.0009(6)	0.1436(4)	0.099(4)	0.083(3)	0.084(4)	–0.051(3)	0.005(3)	–0.021(3)
C(12)	2*i*	0.8028(6)	–0.0382(7)	0.0609(5)	0.093(4)	0.101(4)	0.104(5)	–0.047(3)	0.006(3)	–0.050(4)
C(13)	2*i*	0.8161(6)	0.0392(8)	–0.0161(4)	0.081(3)	0.133(5)	0.077(4)	–0.049(3)	0.004(3)	–0.048(4)
C(14)	2*i*	0.8271(5)	0.1565(6)	–0.0108(4)	0.070(3)	0.103(4)	0.060(3)	–0.032(3)	0.001(2)	–0.026(3)
C(15)	2*i*	0.8247(4)	0.1916(5)	0.0720(3)	0.053(2)	0.081(3)	0.051(2)	–0.029(2)	0.004(2)	–0.018(2)
C(16)	2*i*	0.8367(4)	0.3151(4)	0.0848(3)	0.048(2)	0.074(2)	0.049(2)	–0.027(2)	0.001(2)	–0.006(2)
C(17)	2*i*	0.8372(4)	0.4147(5)	0.0159(3)	0.061(2)	0.090(3)	0.050(2)	–0.027(2)	–0.003(2)	0.004(2)
C(18)	2*i*	0.8476(5)	0.5255(5)	0.0359(4)	0.063(3)	0.074(3)	0.080(3)	–0.027(2)	–0.001(2)	0.009(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(19)	2*i*	0.8576(5)	0.5354(5)	0.1246(4)	0.064(2)	0.062(2)	0.096(4)	–0.029(2)	0.007(2)	–0.007(2)
C(20)	2*i*	0.8570(4)	0.4336(5)	0.1892(3)	0.062(2)	0.071(3)	0.064(3)	–0.029(2)	0.005(2)	–0.012(2)
C(21)	2*i*	0.5167(4)	0.7572(4)	0.1217(3)	0.051(2)	0.052(2)	0.061(2)	–0.023(2)	–0.004(2)	–0.013(2)
C(22)	2*i*	0.5100(4)	0.6347(4)	0.1410(3)	0.059(2)	0.054(2)	0.048(2)	–0.026(2)	–0.001(2)	–0.010(2)
C(23)	2*i*	0.5060(3)	0.5692(3)	0.0721(3)	0.046(2)	0.045(2)	0.050(2)	–0.021(1)	–0.001(1)	–0.008(1)
C(24)	2*i*	0.5094(3)	0.6277(4)	–0.0181(2)	0.049(2)	0.048(2)	0.045(2)	–0.021(1)	0.000(1)	–0.010(1)
C(25)	2*i*	0.5224(4)	0.7481(4)	–0.0369(3)	0.069(2)	0.052(2)	0.052(2)	–0.030(2)	–0.002(2)	–0.002(2)
C(26)	2*i*	0.5258(4)	0.8134(4)	0.0329(3)	0.067(2)	0.053(2)	0.062(2)	–0.031(2)	–0.005(2)	–0.007(2)
C(27)	2*i*	0.5026(4)	0.4365(4)	0.0935(3)	0.056(2)	0.047(2)	0.045(2)	–0.022(2)	0.002(1)	–0.009(1)
C(28)	2*i*	0.2385(4)	0.4793(4)	0.3772(3)	0.051(2)	0.055(2)	0.060(2)	–0.026(2)	–0.006(2)	–0.013(2)
C(29)	2*i*	0.3623(4)	0.4843(4)	0.3582(3)	0.057(2)	0.053(2)	0.049(2)	–0.025(2)	–0.000(2)	–0.006(2)
C(30)	2*i*	0.4287(3)	0.4904(3)	0.4283(2)	0.050(2)	0.046(2)	0.047(2)	–0.022(1)	–0.002(1)	–0.009(1)
C(31)	2*i*	0.3717(4)	0.4928(4)	0.5165(3)	0.052(2)	0.051(2)	0.047(2)	–0.023(2)	0.001(2)	–0.009(2)
C(32)	2*i*	0.2506(4)	0.4804(5)	0.5349(3)	0.053(2)	0.076(3)	0.055(2)	–0.031(2)	0.006(2)	–0.016(2)
C(33)	2*i*	0.1849(4)	0.4738(5)	0.4647(3)	0.056(2)	0.078(3)	0.065(3)	–0.035(2)	0.003(2)	–0.022(2)
C(34)	2*i*	0.4373(4)	0.5072(4)	0.5916(3)	0.051(2)	0.051(2)	0.048(2)	–0.021(2)	0.002(1)	–0.009(1)

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