Crystal structure of bis((pyridyl)amino-iodobenzeno)disulfatodicopper(II) methanol disolvate, $Cu_2(C_{16}H_{12}IN_3)_2(SO_4)_2 \cdot 2CH_3OH$

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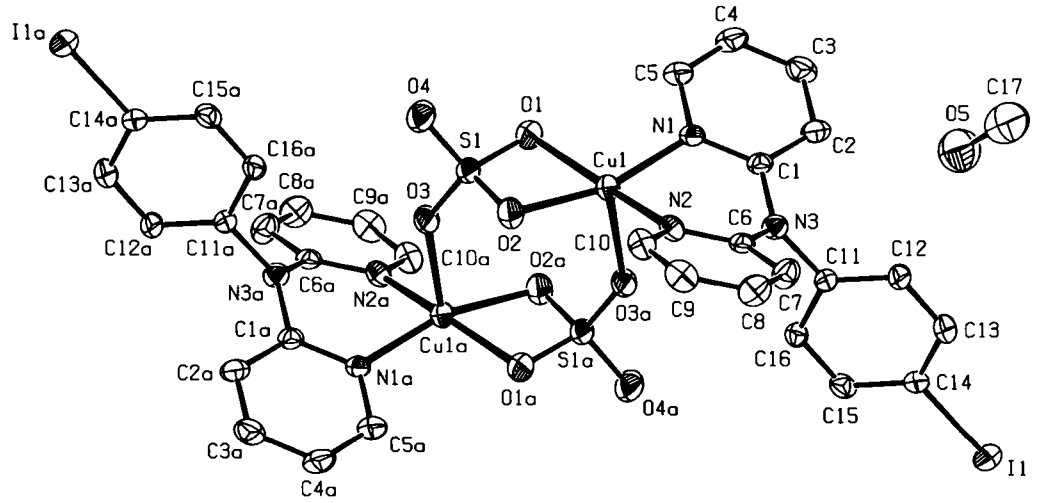

Abstract

$C_{34}H_{32}Cu_2I_2N_6O_{10}S_2$, monoclinic, $P12_1/c1$ (no. 14), a = 8.028(3) Å, b = 12.957(3) Å, c = 18.236(4) Å, β = 95.54(4)°, V = 1888.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F)$ = 0.041, T = 295 K.

Source of material

The ligand 1-iodo-4-[bis(2-pyridyl)amino]benzene (Ibdpam) was synthesized according to the standard Ullmann procedure (cf. [1]). The title complex was obtained by stirring a slight excess of Ibdpam (0.447 g, 1.2 mmol) with 0.244 g (1 mmol) of $CuSO_4 \cdot 5H_2O$ in a 20 mL ethanol-water solution (1:1, *v/v*) for twenty four hours. The final blue-green solution was distilled to dryness, forming a blue precipitate. This was washed several times with chloroform and ether to remove the excess of the ligand and finally recrystallized from methanol (yield 89 % with respect to $CuSO_4 \cdot 5H_2O$). Crystals of the title compound were obtained after recrystallization and slow evaporation in methanol-water solution at ambient temperature. They were air and X-ray stable.

Discussion

The copper(II)(chelate)$_n$(dianion) complexes formulated as Cu(chelate)$_n$*X* with chelate being 2,2′-bipyridyl (bipy), n = 1,2 and *X* as various dianions, coordinated or not, are known to display a large variation of non-regular stereochemistry, presenting a large number of investigated structural data [2-4]. When the coordinated ligand is the more flexible bis(2-pyridyl)-amine, structural data are more limited [5-7]. Moreover, structural data of copper(II) complexes with *N*-substituted dpam chelates are rather rare [8,9]. In the case *X* represents CO_3^{2-} or SO_4^{2-}, several classes of local molecular structures like monomeric, dimeric or polymeric square pyramids with unidentate, bidentate or tridentate oxy-dianions were established [10].

The unit cell of the title crystal structure contains two dinuclear neutral Cu(II) complexes and four methanol molecules. Each metal cation is bonded to one ligand Ibdpam in a bidentate chelating mode and to two oxygen atoms of the sulfate anion. One further oxygen atom from a neighboring sulfate anion is finally coordinated to the copper ion resulting in a square based distorted pyramidal environment. The final coordination mode of each oxy-dianion is tridentate. The Cu1···Cu1a distance is 4.539(1) Å showing no interaction between them. The bond distances and the bite angle of Ibdpam as well as the remaining coordination distances and angles are similar to those found for other analogous copper complexes [5-11]. The square pyramidal base is formed from N1, N2, O1 and O2 atoms, while the axial position is occupied by O3a. The atoms forming the basal plane practically present no deviation from the planarity (smaller or equal than the e.s.d.). The Cu atom is placed 0.199(4) Å above this plane, while the apical O3a atom has a distance of 1.165(4) Å. Each pyridyl ring as well as the phenyl ring of the Ibdpam ligand are planar as expected. The angle between the best planes of the two pyridyl rings is 146.59(4)°. Considering a mean plane passing through the two pyridyl rings, the phenyl ring is nearly perpendicular to this plane forming an angle of 91.06(4)°. The Ibdpam ligand presents a propeller-like geometry. The N3 atom is located in the plane formed by C1, C6 and C11 with a deviation equal to the e.s.d. Hydrogen bonding is present between the alcoholic hydrogen atoms of the methanol molecules, the neighboring iodine and the non-coordinated oxygen atoms of the sulfate anions. The distances between the involved atoms are 2.738(8) Å for O5···O4 and 3.027(6) Å for O5···I1.

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Table 1. Data collection and handling.

Crystal:	blue-green prism, size 0.09 x 0.15 x 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.38 cm^{-1}
Diffractometer, scan mode:	Philips-Stoe, $\omega/2\theta$
$2\theta_{max}$:	52.81°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6007, 3859
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2731
$N(param)_{refined}$:	253
Programs:	SIR2004 [12], CRYSTALS [13]

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

Atom	Site	x	y	z	U_{iso}
H(13)	4e	0.9051	0.3181	0.9868	0.100
H(14)	4e	0.7392	0.3091	0.9151	0.100
H(15)	4e	0.8920	0.4083	0.9130	0.100
H(16)	4e	1.0337	0.2861	0.8552	0.100
H(4)	4e	0.6316	0.2957	0.5516	0.059
H(3)	4e	0.8264	0.3907	0.6186	0.067
H(2)	4e	0.8798	0.3591	0.7420	0.060
H(1)	4e	0.7149	0.2478	0.7968	0.052
H(8)	4e	0.0499	0.0943	0.5771	0.057
H(7)	4e	–0.1338	0.0713	0.6614	0.065
H(6)	4e	–0.0411	0.0729	0.7833	0.063
H(5)	4e	0.2288	0.1112	0.8182	0.058
H(12)	4e	0.6148	–0.0406	0.7357	0.045
H(11)	4e	0.7528	–0.1387	0.8274	0.049
H(10)	4e	0.6353	0.0664	0.9739	0.060
H(9)	4e	0.5193	0.1704	0.8811	0.054

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)	4e	0.40282(7)	0.12956(4)	0.56797(3)	0.0535(3)	0.0360(3)	0.0314(3)	–0.0003(2)	0.0084(2)	–0.0035(2)
I(1)	4e	0.83755(5)	–0.13285(3)	0.99460(2)	0.0674(2)	0.0443(2)	0.0430(2)	–0.0010(1)	–0.0035(1)	0.0108(1)
S(1)	4e	0.3727(2)	0.09982(9)	0.42776(6)	0.0678(7)	0.0338(5)	0.0309(4)	0.0083(5)	0.0053(4)	–0.0018(4)
O(1)	4e	0.5027(5)	0.1597(3)	0.4746(2)	0.070(2)	0.052(2)	0.038(2)	–0.011(2)	0.012(2)	–0.000(1)
O(2)	4e	0.2572(5)	0.0705(3)	0.4837(2)	0.058(2)	0.053(2)	0.041(2)	0.000(2)	0.004(1)	–0.006(1)
O(3)	4e	0.4444(5)	0.0093(3)	0.3969(2)	0.076(2)	0.038(2)	0.037(2)	0.017(2)	0.006(2)	–0.006(1)
O(4)	4e	0.2915(6)	0.1633(3)	0.3703(2)	0.102(3)	0.052(2)	0.043(2)	0.024(2)	0.002(2)	0.003(2)
O(5)	4e	0.9779(8)	0.2612(5)	0.8849(4)	0.102(4)	0.107(5)	0.103(4)	–0.005(4)	0.002(3)	0.002(4)
C(1)	4e	0.5758(5)	0.2051(3)	0.7053(2)	0.040(2)	0.025(2)	0.035(2)	0.005(2)	0.005(1)	0.004(1)
C(2)	4e	0.7003(6)	0.2581(3)	0.7478(3)	0.052(2)	0.032(2)	0.047(2)	–0.005(2)	0.002(2)	0.010(2)
C(3)	4e	0.7956(7)	0.3264(4)	0.7152(3)	0.056(3)	0.040(3)	0.060(3)	–0.014(2)	–0.005(2)	–0.001(2)
C(4)	4e	0.7677(7)	0.3425(4)	0.6406(3)	0.070(3)	0.042(3)	0.053(3)	–0.009(2)	0.016(2)	0.014(2)
C(5)	4e	0.6467(7)	0.2874(4)	0.6007(3)	0.068(3)	0.035(2)	0.047(2)	–0.010(2)	0.011(2)	0.006(2)
C(6)	4e	0.3037(5)	0.1173(3)	0.7163(2)	0.043(2)	0.021(2)	0.036(2)	0.004(1)	0.007(2)	0.002(1)
C(7)	4e	0.1930(6)	0.1041(4)	0.7701(3)	0.046(2)	0.059(3)	0.040(2)	–0.007(2)	0.007(2)	0.006(2)
C(8)	4e	0.0296(6)	0.0855(4)	0.7490(3)	0.043(3)	0.062(3)	0.056(3)	–0.003(2)	0.014(2)	0.006(2)
C(9)	4e	–0.0245(6)	0.0815(4)	0.6755(3)	0.039(2)	0.053(3)	0.066(3)	0.005(2)	0.007(2)	–0.007(2)
C(10)	4e	0.0861(6)	0.0976(4)	0.6254(3)	0.049(3)	0.050(3)	0.048(2)	0.001(2)	0.001(2)	–0.008(2)
C(11)	4e	0.5513(5)	0.0743(3)	0.7999(2)	0.040(2)	0.030(2)	0.028(2)	–0.006(2)	0.004(1)	0.001(1)
C(12)	4e	0.5598(7)	0.1078(4)	0.8710(2)	0.078(3)	0.032(2)	0.029(2)	0.009(2)	0.004(2)	–0.003(2)
C(13)	4e	0.6380(7)	0.0474(4)	0.9266(2)	0.082(4)	0.042(2)	0.033(2)	0.002(2)	0.006(2)	–0.010(2)
C(14)	4e	0.7129(6)	–0.0441(3)	0.9096(2)	0.053(2)	0.028(2)	0.035(2)	–0.004(2)	0.006(2)	0.004(2)
C(15)	4e	0.7056(5)	–0.0784(3)	0.8384(2)	0.043(2)	0.030(2)	0.042(2)	0.002(2)	0.010(2)	–0.005(2)
C(16)	4e	0.6227(5)	–0.0187(3)	0.7828(2)	0.045(2)	0.034(2)	0.029(2)	–0.005(2)	0.011(2)	–0.004(1)
C(17)	4e	0.871(1)	0.3283(8)	0.9281(5)	0.081(5)	0.116(7)	0.111(7)	–0.034(5)	–0.037(5)	0.027(6)
N(1)	4e	0.5516(5)	0.2189(3)	0.6329(2)	0.052(2)	0.025(2)	0.035(2)	–0.001(1)	0.009(1)	0.001(1)
N(2)	4e	0.2511(4)	0.1148(3)	0.6456(2)	0.037(2)	0.033(2)	0.039(2)	0.002(1)	0.005(1)	–0.007(1)
N(3)	4e	0.4732(4)	0.1350(3)	0.7389(2)	0.034(2)	0.036(2)	0.038(2)	–0.003(1)	0.003(1)	0.002(1)

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