Crystal structure of dichlorobis(dimethylsulfoxide-*O*)-bis-(isonicotinic acid-*N*)copper(II) — dimethylsulfoxide (1:2), $[CuCl_2(C_6H_5NO_2)_2(C_2H_6OS)_2]_2 \cdot 2C_2H_6OS$

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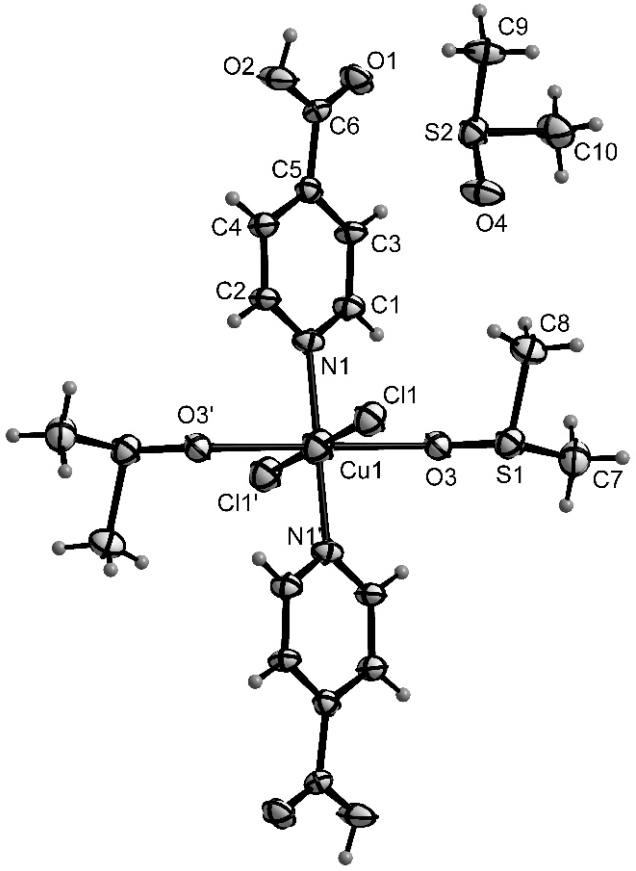

Abstract

$C_{20}H_{34}Cl_2CuN_2O_8S_4$, triclinic, $P\bar{1}$ (no. 2), a = 7.105(5) Å, b = 10.578(7) Å, c = 11.007(7) Å, α = 71.58(1)°, β = 84.51(2)°, γ = 77.47(2)°, V = 765.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.155, T = 296 K.

Source of material

The title complex was synthesized from a mixture of $CuCl_2$ (0.120 g, 0.9 mmol), isonicotinic acid (0.111 g, 0.9 mmol) and DMSO (1.0 ml) sealed in a pyrex tube, heated to 100 °C for 68 hours, and then cooled to room temperature at 10 °C/h. The pH value of the solution before and after the reaction was 7 and 5, respectively. The solid products were recovered by vacuum filtration and washed with DMSO. Pale green rod-like crystals were obtained as a single phase. The product was slightly unstable in air. The yield was about 48 % based on copper. EDS analysis confirmed the presence of Cu and Cl.

Experimental details

All the hydrogen atoms associated with the isonicotinic acid and DMSO molecules were placed geometrically and refined as riding.

Discussion

The crystal structure of the title compound comprise discrete centrosymmetric mononuclear $CuCl_2$(isonicotinic acid)$_2$(DMSO)$_2$ and lattice DMSO molecules. The crystallographically unique Cu atom is coordinated by two chlorine atoms (d(Cu—Cl) = 2.335(2) Å), and two nitogen atoms from different isonicotinic acid molecules (d(Cu—N) = 1.987(4) Å). The additional oxygen atoms of two DMSO molecules (d(Cu—O) = 2.453(3) Å) complete an octahedral environment of Cu. The bond valence sum (BVS) calculation for Cu gives a value of +1.78, indicating an oxidation state of +2. The copper atom lies on a crystallographic inversion center so that ∠N–Cu–N, ∠Cl–Cu–Cl and ∠O–Cu–O are 180°. Also, two pyridine rings are coplanar, however, they are not parellel with either CuN_2Cl_2 or CuN_2O_2 planes, with the torsion angles of C2–N1–Cu1–Cl1 = 115.45(4)° and C2–N1–Cu1–O3 = 154.81(4)°. The carboxylic acid group has to be conjugated and therefore is coplanar as shown by the torsion angle C4–C5–C6–C2 = –1.3°. The lattice DMSO molecules form hydrogen bonds to the carboxyl groups in the $CuCl_2$(isonicotinic acid)$_2$(DMSO)$_2$ molecules. The DMSO molecule serves as a strong hydrogen bond acceptor, as indicated by the hydrogen bonding between the OH groups in the complex and the S=O groups in DMSO with d(H···O) = 1.712(9) Å, ∠O–H···O = 169.01(4)°, d(O···O) = 2.541(1) Å. Several coordination complexes containing isonicotinic acids and chlorine atoms are reported, and examples include Cu(I)Cl(isonicotinic acid), Pd(II)Cl$_2$- (isonicotinic acid)$_2$, and Pd(II)Cl$_2$(isonicotinic acid)$_2 \cdot$ 2DMSO [1-3]. The complex Pd(II)Cl$_2$(isonicotinic acid)$_2 \cdot$ 2DMSO has lattice DMSO molecules, and it shows similar hydrogen bonding between the isonicotinic acid in Pd(II)Cl$_2$(isonicotinic acid)$_2$ and the lattice DMSO molecules as found in the title complex [3].

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Table 1. Data collection and handling.

Crystal:	green rod, size 0.18 × 0.20 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.03 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, φ/ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6323, 3417
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1715
$N(param)_{refined}$:	174
Programs:	SHELXS-97, SHELXL-97 [4], DIAMOND [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.7748	0.1626	0.4994	0.107
H(1)	2*i*	–0.0302	0.3142	0.2678	0.049
H(2A)	2*i*	0.4178	0.4003	0.0458	0.047
H(3)	2*i*	0.1629	0.2020	0.4386	0.045
H(4)	2*i*	0.6213	0.2863	0.2094	0.049
H(7A)	2*i*	0.3646	0.6098	0.2452	0.103
H(7B)	2*i*	0.4109	0.6809	0.3409	0.103
H(7C)	2*i*	0.4823	0.5238	0.3678	0.103
H(8A)	2*i*	0.8231	0.5140	0.4037	0.100
H(8B)	2*i*	0.7859	0.6693	0.3905	0.100
H(8C)	2*i*	0.9594	0.6057	0.3151	0.100
H(9A)	2*i*	–0.2565	–0.0443	0.2441	0.090
H(9B)	2*i*	–0.1015	–0.0967	0.1507	0.090
H(9C)	2*i*	–0.1871	0.0592	0.1205	0.090
H(10A)	2*i*	0.2028	0.0737	0.0877	0.112
H(10B)	2*i*	0.2376	–0.0853	0.1273	0.112
H(10C)	2*i*	0.3467	–0.0145	0.1961	0.112

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)	1*c*	0	½	0	0.0432(4)	0.0321(6)	0.0349(4)	–0.0074(4)	–0.0121(3)	–0.0018(3)
Cl(1)	2*i*	0.1082(2)	0.6839(1)	0.02365(9)	0.0531(7)	0.0389(8)	0.0446(5)	–0.0141(6)	–0.0072(5)	–0.0076(5)
O(1)	2*i*	0.4748(5)	0.1244(4)	0.5652(2)	0.059(2)	0.070(3)	0.031(1)	–0.015(2)	0.001(1)	–0.003(2)
O(2)	2*i*	0.7173(5)	0.1839(5)	0.4325(3)	0.037(2)	0.126(5)	0.037(2)	–0.015(2)	–0.011(1)	–0.004(2)
N(1)	2*i*	0.1711(5)	0.3768(4)	0.1398(3)	0.045(2)	0.032(3)	0.036(2)	–0.010(2)	–0.007(2)	–0.004(2)
C(1)	2*i*	0.1018(6)	0.3120(6)	0.2568(4)	0.038(2)	0.045(4)	0.040(2)	–0.013(3)	–0.003(2)	–0.009(2)
C(2)	2*i*	0.3654(6)	0.3618(5)	0.1264(3)	0.035(2)	0.048(4)	0.030(2)	–0.008(2)	–0.008(2)	–0.002(2)
C(3)	2*i*	0.2173(6)	0.2432(5)	0.3596(3)	0.035(2)	0.039(3)	0.032(2)	–0.009(2)	–0.008(2)	0.001(2)
C(4)	2*i*	0.4889(6)	0.2936(6)	0.2240(3)	0.035(2)	0.045(4)	0.037(2)	–0.006(2)	–0.007(2)	–0.005(2)
C(5)	2*i*	0.4148(6)	0.2351(5)	0.3456(3)	0.043(2)	0.034(3)	0.033(2)	–0.005(2)	–0.004(2)	–0.009(2)
C(6)	2*i*	0.5352(6)	0.1741(5)	0.4591(4)	0.037(2)	0.036(3)	0.037(2)	0.005(2)	–0.009(2)	–0.008(2)
S(1)	2*i*	0.6777(2)	0.6390(2)	0.2145(1)	0.0581(8)	0.042(1)	0.0487(6)	–0.0045(7)	–0.0060(6)	–0.0110(6)
O(3)	2*i*	–0.2606(5)	0.5244(4)	0.1590(3)	0.054(2)	0.052(3)	0.039(1)	–0.009(2)	–0.004(1)	–0.017(2)
C(7)	2*i*	0.4585(8)	0.6100(8)	0.3023(5)	0.063(4)	0.073(6)	0.076(3)	–0.009(4)	0.008(3)	–0.037(3)
C(8)	2*i*	0.8289(8)	0.6028(8)	0.3461(5)	0.064(3)	0.080(6)	0.065(3)	–0.013(4)	–0.013(3)	–0.032(3)
S(2)	2*i*	0.9636(2)	0.0078(2)	0.7260(1)	0.0573(8)	0.057(1)	0.0458(6)	–0.0167(8)	–0.0032(6)	–0.0165(6)
O(4)	2*i*	0.0843(5)	–0.1438(5)	0.3759(3)	0.064(2)	0.085(4)	0.041(2)	–0.029(3)	–0.012(2)	0.004(2)
C(9)	2*i*	–0.1482(8)	–0.0243(7)	0.1875(4)	0.071(4)	0.050(4)	0.051(2)	–0.016(3)	–0.016(2)	0.002(2)
C(10)	2*i*	0.2278(8)	–0.0086(8)	0.1580(4)	0.063(4)	0.099(7)	0.051(3)	–0.022(4)	0.005(3)	–0.005(3)

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