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Crystal structure of bis(2,5-bis(2-pyridyl)-1,3,4-thiadiazole)bis(perchlorato)copper(II), $Cu(C_{12}H_8N_4S)_2(ClO_4)_2$

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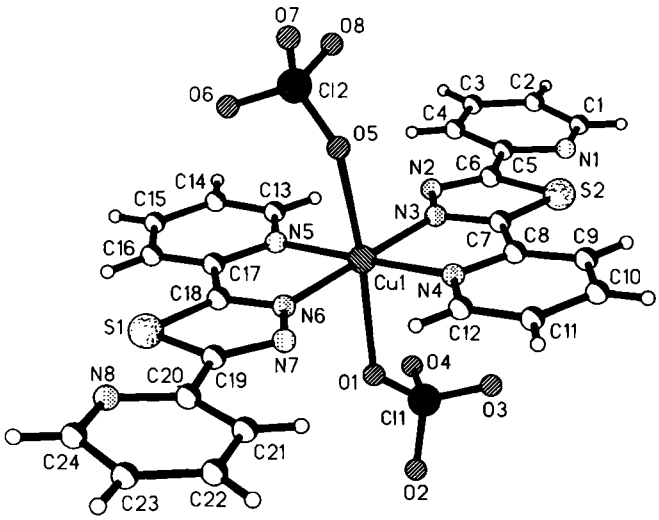

Abstract

$C_{24}H_{16}Cl_2CuN_8O_8S_2$, monoclinic, $P12_1/c1$ (no. 14), a = 16.422(1) Å, b = 8.9970(7) Å, c = 19.636(2) Å, β = 93.284(1)°, V = 2896.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.139, T = 291 K.

Source of material

The ligand 1,3,4-thiadiazole-2,5-di-2-pyridyl was prepared according to the literature procedure [1]. The ligand (0.024 g, 0.1 mmol) dissolved in 5 ml chloroform was added to 10 ml methanol solution of copper acetate (0.020 g, 0.1 mmol) while stirring. The ammonium perchlorate solution (0.024 g, 0.2 mmol) in 5 ml water was added dropwise after 20 min. Suitable blue block crystals were obtained by slow evaporation of the solvents in about 40 days (yield 35 %).

Discussion

The compound 1,3,4-thiadiazole-2,5-di-2-pyridyl was usually used as bidentate ligand to form five-atomic ring complexes and sometimes it coordinates two metal atoms by four nitrogen atoms as double-bidentate ligand [2]. In the mononuclear or dinuclear complexes, the metal atoms are coordinated with NO_3^- anions or water molecules but seldom with perchlorate anions [3,4].

We supposed that the perchlorate anion only acts as counter anion, but X-ray diffraction experiment has it shown also as coordinating ligand. The central copper ion is hexa-coordinated by four nitrogen atoms of two distinct 1,3,4-thiadiazole-2,5-di-2-pyridyl molecules and two oxygen atoms from two perchlorate anions to form a octahedral environment. Selected bond lengths and angles (d(Cu1—N3) = 2.022(2) Å, d(Cu1—N4) = 2.041(2) Å, d(Cu1—N5) = 2.031(2) Å, d(Cu1—N6) = 2.030(2) Å, d(Cu1—O1) = 2.374(3) Å, d(Cu1—O5) = 2.433(3) Å; ∠N3–Cu1–N5 = 99.7(1)°, ∠N3–Cu1–N4 = 80.8(1)°, ∠N3–Cu1–O1 = 95.2(1)°, ∠N6–Cu1–O1 = 84.7(1)°) give evidences for a distortion of the ideal octahedron. In the unit cell, there exist stacking interactions between two pyridyl rings from two different ligands. Six aromatic ring atoms (C1, C2, C3, C4, C5, N1) form medium strong π-π stacking with the ring atoms (C13, C14, C15, C16, C17, N5) in a neighboring molecule with a centroid distance of 3.548 Å and a dihedral angle of 8.1°. This stacking along the a axis led a one-dimensional chain-like structure.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.17 × 0.32 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.47 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24855, 6661
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5036
$N(param)_{refined}$:	406
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	–0.0801	0.9994	–0.2392	0.077
H(2)	4e	–0.1690	1.0586	–0.1568	0.084
H(3)	4e	–0.1441	0.9672	–0.0464	0.082
H(4)	4e	–0.0269	0.8244	–0.0220	0.066
H(9)	4e	0.3114	0.6717	–0.2281	0.053
H(10)	4e	0.4377	0.5625	–0.2426	0.057
H(11)	4e	0.4955	0.4154	–0.1561	0.063
H(12)	4e	0.4288	0.3836	–0.0569	0.058
H(13)	4e	0.0977	0.5965	0.0575	0.058
H(14)	4e	0.0356	0.5772	0.1594	0.066
H(15)	4e	0.0930	0.4288	0.2454	0.061
H(16)	4e	0.2154	0.3074	0.2280	0.053
H(21)	4e	0.5479	0.1462	0.0170	0.063
H(22)	4e	0.6685	0.0136	0.0399	0.075
H(23)	4e	0.7004	–0.0665	0.1509	0.080
H(24)	4e	0.6127	–0.0140	0.2342	0.074

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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}
Cu(1)	4e	0.26150(2)	0.48653(4)	−0.00085(2)	0.0382(2)	0.0439(2)	0.0239(2)	0.0050(2)	0.0046(1)	0.0052(1)
Cl(1)	4e	0.14664(5)	0.2451(1)	−0.10480(4)	0.0499(5)	0.0533(5)	0.0477(5)	0.0009(4)	−0.0031(4)	−0.0091(4)
Cl(2)	4e	0.34185(6)	0.7706(1)	0.10816(5)	0.0580(5)	0.0547(5)	0.0483(5)	−0.0064(4)	0.0045(4)	−0.0109(4)
S(1)	4e	0.36793(5)	0.21898(9)	0.17003(4)	0.0501(5)	0.0471(4)	0.0308(4)	0.0074(3)	0.0048(3)	0.0099(3)
S(2)	4e	0.15683(5)	0.75346(9)	−0.17247(4)	0.0470(4)	0.0453(4)	0.0312(4)	0.0046(3)	0.0016(3)	0.0085(3)
O(1)	4e	0.2011(2)	0.2660(3)	−0.0469(2)	0.121(3)	0.068(2)	0.064(2)	−0.031(2)	−0.028(2)	0.000(2)
O(2)	4e	0.1396(3)	0.0951(4)	−0.1175(2)	0.171(4)	0.067(2)	0.133(3)	−0.044(3)	−0.007(3)	−0.029(2)
O(3)	4e	0.1795(3)	0.3178(5)	−0.1606(2)	0.188(4)	0.100(3)	0.048(2)	−0.051(3)	0.001(2)	−0.004(2)
O(4)	4e	0.0740(3)	0.3070(8)	−0.0884(3)	0.090(3)	0.273(7)	0.210(5)	0.102(4)	0.033(3)	0.052(5)
O(5)	4e	0.3486(3)	0.6769(4)	0.0529(2)	0.161(4)	0.107(3)	0.085(2)	−0.076(3)	0.045(2)	−0.048(2)
O(6)	4e	0.3101(4)	0.6969(6)	0.1620(2)	0.279(6)	0.160(4)	0.047(2)	−0.139(4)	0.016(3)	−0.012(2)
O(7)	4e	0.4155(3)	0.8401(5)	0.1250(2)	0.125(4)	0.124(3)	0.149(4)	−0.066(3)	−0.023(3)	−0.021(3)
O(8)	4e	0.2911(4)	0.8844(8)	0.0869(4)	0.181(6)	0.222(7)	0.278(7)	0.132(5)	0.078(5)	0.061(6)
N(1)	4e	−0.0012(2)	0.8875(3)	−0.1817(1)	0.039(2)	0.058(2)	0.049(2)	0.002(1)	0.001(1)	0.013(1)
N(2)	4e	0.1160(2)	0.6887(3)	−0.0519(1)	0.043(1)	0.046(2)	0.037(1)	0.008(1)	0.004(1)	0.004(1)
N(3)	4e	0.1910(2)	0.6264(3)	−0.0593(1)	0.042(1)	0.042(1)	0.029(1)	0.005(1)	0.005(1)	0.002(1)
N(4)	4e	0.3326(2)	0.5049(3)	−0.0823(1)	0.042(1)	0.041(1)	0.027(1)	0.001(1)	0.005(1)	0.001(1)
N(5)	4e	0.1931(2)	0.4724(3)	0.0819(1)	0.039(1)	0.043(1)	0.026(1)	0.001(1)	0.003(1)	0.002(1)
N(6)	4e	0.3326(2)	0.3458(3)	0.0574(1)	0.041(1)	0.047(2)	0.027(1)	0.003(1)	0.004(1)	0.003(1)
N(7)	4e	0.4073(2)	0.2823(3)	0.0491(1)	0.041(1)	0.049(2)	0.036(1)	0.006(1)	0.004(1)	0.005(1)
N(8)	4e	0.5293(2)	0.0905(3)	0.1778(1)	0.046(2)	0.048(2)	0.046(2)	0.003(1)	0.002(1)	0.013(1)
C(1)	4e	−0.0688(2)	0.9660(5)	−0.1949(2)	0.049(2)	0.076(3)	0.066(2)	0.010(2)	−0.004(2)	0.025(2)
C(2)	4e	−0.1233(3)	1.0006(5)	−0.1458(3)	0.046(2)	0.073(3)	0.092(3)	0.017(2)	0.003(2)	0.016(2)
C(3)	4e	−0.1081(3)	0.9471(5)	−0.0801(2)	0.051(2)	0.079(3)	0.077(3)	0.014(2)	0.017(2)	0.001(2)
C(4)	4e	−0.0385(2)	0.8631(4)	−0.0654(2)	0.053(2)	0.063(2)	0.051(2)	0.007(2)	0.008(2)	0.007(2)
C(5)	4e	0.0130(2)	0.8391(3)	−0.1176(2)	0.038(2)	0.039(2)	0.049(2)	−0.001(1)	0.002(1)	0.005(1)
C(6)	4e	0.0904(2)	0.7585(3)	−0.1070(2)	0.040(2)	0.036(2)	0.033(1)	−0.001(1)	0.002(1)	0.001(1)
C(7)	4e	0.2199(2)	0.6507(3)	−0.1188(1)	0.044(2)	0.033(1)	0.029(1)	−0.001(1)	0.001(1)	−0.000(1)
C(8)	4e	0.2993(2)	0.5887(3)	−0.1334(1)	0.042(2)	0.033(1)	0.028(1)	−0.002(1)	0.003(1)	−0.001(1)
C(9)	4e	0.3363(2)	0.6129(4)	−0.1940(2)	0.056(2)	0.046(2)	0.029(1)	−0.001(2)	0.005(1)	0.003(1)
C(10)	4e	0.4110(2)	0.5479(4)	−0.2026(2)	0.056(2)	0.055(2)	0.034(2)	−0.002(2)	0.018(1)	−0.003(1)
C(11)	4e	0.4454(2)	0.4611(4)	−0.1511(2)	0.050(2)	0.060(2)	0.049(2)	0.010(2)	0.017(2)	0.003(2)
C(12)	4e	0.4048(2)	0.4421(4)	−0.0916(2)	0.049(2)	0.058(2)	0.039(2)	0.013(2)	0.009(1)	0.010(2)
C(13)	4e	0.1223(2)	0.5394(4)	0.0924(2)	0.047(2)	0.060(2)	0.040(2)	0.010(2)	0.006(1)	0.008(2)
C(14)	4e	0.0840(2)	0.5268(4)	0.1533(2)	0.053(2)	0.068(2)	0.046(2)	0.016(2)	0.015(2)	0.007(2)
C(15)	4e	0.1183(2)	0.4395(4)	0.2045(2)	0.056(2)	0.062(2)	0.036(2)	0.003(2)	0.017(1)	0.003(2)
C(16)	4e	0.1910(2)	0.3678(4)	0.1942(2)	0.055(2)	0.050(2)	0.029(1)	0.002(2)	0.008(1)	0.006(1)
C(17)	4e	0.2264(2)	0.3878(3)	0.1329(1)	0.040(2)	0.035(1)	0.031(1)	−0.002(1)	0.004(1)	−0.002(1)
C(18)	4e	0.3045(2)	0.3223(3)	0.1173(1)	0.043(2)	0.037(2)	0.028(1)	−0.003(1)	0.001(1)	0.002(1)
C(19)	4e	0.4337(2)	0.2127(3)	0.1040(2)	0.040(2)	0.039(2)	0.033(1)	−0.002(1)	0.000(1)	0.003(1)
C(20)	4e	0.5117(2)	0.1341(3)	0.1138(2)	0.040(2)	0.039(2)	0.041(2)	−0.003(1)	0.000(1)	0.004(1)
C(21)	4e	0.5619(2)	0.1109(4)	0.0606(2)	0.052(2)	0.061(2)	0.046(2)	0.004(2)	0.008(2)	0.006(2)
C(22)	4e	0.6335(2)	0.0334(5)	0.0745(2)	0.048(2)	0.074(3)	0.068(2)	0.009(2)	0.017(2)	0.002(2)
C(23)	4e	0.6525(3)	−0.0141(5)	0.1403(2)	0.048(2)	0.065(2)	0.087(3)	0.015(2)	0.006(2)	0.016(2)
C(24)	4e	0.5992(3)	0.0174(4)	0.1898(2)	0.058(2)	0.066(2)	0.061(2)	0.007(2)	−0.003(2)	0.021(2)

References

1. Mounim, L.; Fouad, B.; Michel, L.: Rapid synthesis of 2,5-disubstituted 1,3,4-thiadiazoles under microwave irradiation. J. Heterocyclic Chem. **42** (2005) 991-994.
2. Bentiss, F.; Lagrenee, M.; Mentre, O.; Conflant, P.; Vezin, H.; Wignacour, J. P.; Holt, E. M.: Intermolecular magnetic couplings in the dinuclear copper(II) complex μ-chloro-μ-[2,5-bis(2-pyridyl)-1,3,4-thiadiazole] aqua chlorocopper(II) dichlorocopper(II): synthesis, crystal structure and EPR and magnetic characterization. Inorg. Chem. **43** (2004) 1865-1873.
3. Bentiss, F.; Lagrenee, M.; Wignacour, J. P.; Holt, E. M.: Complexes of cobalt(II), nickel(II) and copper(II) with a thia ligand, 2,5-bis(2-pyridyl)-1,3,4-thiadiazole: Structure Identification. Polyhedron **21** (2002) 403-408.
4. Bentiss, F.; Lagrenee, M.; Vezin, H.; Wignacour, J. P.; Holt, E. M.: Syntheses and crystal structures of two mononuclear Zn(II) complexes with the 2,5-bis(2-pyridyl)-1,3,4-thiadiazole ligand. Polyhedron **23** (2004) 1903-1907.
5. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.