Crystal structure of [1-(4-carboxyphenyl)-5-mercapto-1*H*-tetrazole]-bis(1,10-phenanthroline)copper(II) perchlorate — methanol (1:1.5), $[Cu(C_8H_5N_4O_2S)(C_{12}H_8N_2)_2][ClO_4] \cdot 1.5CH_3OH$

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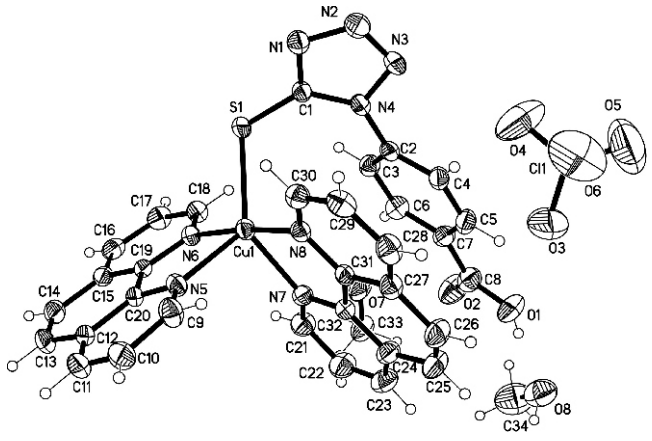

Abstract

$C_{33.5}H_{27}ClCuN_8SO_{7.5}$, triclinic, $P\overline{1}$ (no. 2), a = 9.4707(8) Å, b = 12.4239(8) Å, c = 16.952(1) Å, α = 97.342(5)°, β = 103.227(6)°, γ = 110.257(7)°, V = 1774.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.139, T = 294 K.

Source of material

A mixed solution of 1-(4-carboxyphenyl)-5-mercapto-1*H*-tetrazole (HL, 0.05 mmol), 1,10-phenanthroline (phen, 0.05 mmol) in the presence of excess 2,6-dimethylpyridine (ca. 0.05 mL for adjusting the pH value to basic condition) in CH_3OH (10 mL) was carefully layered on top of a H_2O solution (15 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) in a test tube. After two weeks at room temperature, blue single crystals suitable for X-ray analysis were obtained (yield 40 % based on HL ligand).

Elemental analysis — found: C, 50.76 %; H, 3.43 %; N, 14.14 %; calculated for $C_{33.5}H_{27}ClCuN_8SO_{7.5}$: C, 50.60 %; H, 3.72 %; N, 14.30 %.

Experimental details

We found that the thermal vibration parameters of C33 and O7 related to the second methanol were obviously higher than those of C34 and O8 for the first methanol. Thus, we changed the occupation for the second methanol from 1.00 to 0.50 manually, which was not further refined by the software. The methanol and water H atoms were refined with the O–H distances fixed at d(O—H) = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(parent O atom). The C-bound H atoms were included in calculated positions and treated as riding atoms with d(C—H) = 0.93 - 0.96 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C).

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Discussion

5-Substituted 1*H*-tetrazoles have demonstrated to be of especial interest and have been widely used to construct various coordination complexes exhibiting great structural diversity, which show rich coordination chemistry, interesting optical, magnetic, and hydrogen-storage properties [1-5]. In addition, the introduction of 2,2-bipyridine bidentate chelating molecule as auxiliary co-ligand into the reaction system may usually generate some interesting coordination architectures [6].

In the title crystal structure, the asymmetric unit consists of one Cu(II) ion, two phen molecules, one L ligand, one ClO_4^- anion, and one and a half free methanol molecules. Each Cu(II) center is penta-coordinated by one S atom from L ligand and four N-atom donors from two phen ligands. Moreover, phen acts as a typical chelating ligand coordinating to the Cu(II) atom with the d(Cu—N) ranging from 1.981(3) to 2.143(4) Å and the ∠N–C–N in the range of 81.22(12) to 173.88(14)°. The L ligand adopts a unidentate coordination mode with d(Cu—S) = 2.327(1) Å.The carboxyl from L ligand and H atoms from phen molecules are involved in intramolecular O–H···O and C–H···O hydrogen bonds, which result in a 3D supramolecular structure. In addition, the structure also contains intramolecular $\pi \cdots \pi$ stacking interactions between the phenyl and pyridine rings of adjacent phen ligands with the centroid-centroid distances of 3.649 - 3.753 Å.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.12 × 0.16 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.11 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12861, 6235
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3743
$N(param)_{refined}$:	482
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7], PLATON [8]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3A)	2*i*		0.5296	0.5599	0.1296	0.053
H(4A)	2*i*		0.7557	0.3739	0.2398	0.051
H(5A)	2*i*		0.7284	0.4445	0.3657	0.061
H(6A)	2*i*		0.5003	0.6288	0.2563	0.060
H(9A)	2*i*		1.3071	0.8165	0.1913	0.069
H(10A)	2*i*		1.5268	0.9855	0.2069	0.079
H(11A)	2*i*		1.4937	1.1491	0.1721	0.076

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(13A)	2*i*		1.3021	1.2472	0.1180	0.076
H(14A)	2*i*		1.0507	1.2321	0.0716	0.073
H(16A)	2*i*		0.7577	1.1133	0.0433	0.064
H(17A)	2*i*		0.5629	0.9419	0.0457	0.065
H(18A)	2*i*		0.6269	0.7912	0.0880	0.055
H(21A)	2*i*		0.8393	0.9027	0.2817	0.066
H(22A)	2*i*		0.8632	0.9264	0.4214	0.081
H(23A)	2*i*		0.9808	0.8260	0.4988	0.081
H(25A)	2*i*		1.1040	0.6705	0.5017	0.078
H(26A)	2*i*		1.1807	0.5450	0.4314	0.076
H(28A)	2*i*		1.2101	0.4563	0.2943	0.068

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(29A)	2*i*		1.1745	0.4487	0.1555	0.064
H(30A)	2*i*		1.0530	0.5602	0.0916	0.055
H(33A)	2*i*	0.5	0.5706	0.9780	0.4073	0.082
H(33B)	2*i*	0.5	0.4664	0.8811	0.4439	0.082
H(33C)	2*i*	0.5	0.3867	0.9337	0.3760	0.082
H(34A)	2*i*		0.5771	0.7784	0.6642	0.156
H(34B)	2*i*		0.4970	0.7292	0.5682	0.156
H(34C)	2*i*		0.6603	0.8359	0.6013	0.156
H(1)	2*i*		0.6574	0.6051	0.5104	0.109
H(7)	2*i*	0.5	0.4394	0.7640	0.3485	0.092
H(8)	2*i*		0.7688	0.7205	0.6334	0.118

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*		0.92780(6)	0.74512(4)	0.14740(3)	0.0411(4)	0.0340(3)	0.0417(3)	0.0138(2)	0.0119(2)	0.0132(2)
C(1)	2*i*		0.7090(5)	0.4702(3)	0.0354(2)	0.035(3)	0.035(2)	0.037(2)	0.010(2)	0.009(2)	0.011(2)
C(2)	2*i*		0.6471(5)	0.4625(3)	0.1741(3)	0.033(3)	0.035(2)	0.041(2)	0.003(2)	0.013(2)	0.007(2)
C(3)	2*i*		0.5698(5)	0.5373(4)	0.1771(3)	0.041(3)	0.048(3)	0.043(3)	0.018(2)	0.011(2)	0.014(2)
C(4)	2*i*		0.7057(5)	0.4261(4)	0.2436(3)	0.042(3)	0.041(2)	0.045(3)	0.015(2)	0.012(2)	0.017(2)
C(5)	2*i*		0.6890(5)	0.4682(4)	0.3186(3)	0.049(3)	0.058(3)	0.046(3)	0.019(3)	0.013(2)	0.024(2)
C(6)	2*i*		0.5530(5)	0.5784(4)	0.2530(3)	0.044(3)	0.057(3)	0.053(3)	0.023(2)	0.016(2)	0.012(2)
C(7)	2*i*		0.6145(5)	0.5451(4)	0.3244(3)	0.041(3)	0.053(3)	0.041(3)	0.011(2)	0.012(2)	0.010(2)
C(8)	2*i*		0.5964(6)	0.5936(5)	0.4039(3)	0.049(3)	0.075(4)	0.054(3)	0.019(3)	0.017(3)	0.019(3)
C(9)	2*i*		1.2927(6)	0.8836(4)	0.1792(3)	0.044(3)	0.058(3)	0.073(3)	0.018(3)	0.021(3)	0.026(3)
C(10)	2*i*		1.4263(6)	0.9850(5)	0.1878(3)	0.040(3)	0.076(4)	0.069(4)	0.008(3)	0.012(3)	0.019(3)
C(11)	2*i*		1.4062(7)	1.0820(4)	0.1678(3)	0.060(4)	0.051(3)	0.060(3)	–0.002(3)	0.024(3)	0.007(3)
C(12)	2*i*		1.2541(6)	1.0821(4)	0.1404(3)	0.052(3)	0.043(3)	0.036(3)	0.000(2)	0.018(2)	0.007(2)
C(13)	2*i*		1.2199(8)	1.1778(4)	0.1157(3)	0.084(5)	0.032(2)	0.060(3)	0.001(3)	0.028(3)	0.012(2)
C(14)	2*i*		1.0700(8)	1.1692(4)	0.0889(3)	0.095(5)	0.034(3)	0.052(3)	0.019(3)	0.025(3)	0.014(2)
C(15)	2*i*		0.9405(6)	1.0655(3)	0.0866(3)	0.067(4)	0.031(2)	0.036(2)	0.018(2)	0.017(2)	0.006(2)
C(16)	2*i*		0.7832(7)	1.0527(4)	0.0610(3)	0.082(4)	0.043(3)	0.040(3)	0.034(3)	0.012(3)	0.009(2)
C(17)	2*i*		0.6678(6)	0.9509(4)	0.0620(3)	0.060(4)	0.057(3)	0.054(3)	0.035(3)	0.012(3)	0.013(2)
C(18)	2*i*		0.7071(6)	0.8603(4)	0.0877(3)	0.044(3)	0.043(2)	0.049(3)	0.016(2)	0.013(2)	0.011(2)
C(19)	2*i*		0.9707(5)	0.9702(3)	0.1106(2)	0.045(3)	0.032(2)	0.029(2)	0.010(2)	0.011(2)	0.006(2)
C(20)	2*i*		1.1283(5)	0.9777(3)	0.1362(2)	0.045(3)	0.033(2)	0.033(2)	0.004(2)	0.015(2)	0.008(2)
C(21)	2*i*		0.8842(6)	0.8592(4)	0.3118(3)	0.068(4)	0.048(3)	0.054(3)	0.029(3)	0.018(3)	0.008(2)
C(22)	2*i*		0.8996(7)	0.8748(4)	0.3962(3)	0.095(5)	0.057(3)	0.056(3)	0.038(3)	0.023(3)	0.005(3)
C(23)	2*i*		0.9679(7)	0.8146(4)	0.4419(3)	0.087(4)	0.069(3)	0.043(3)	0.029(3)	0.018(3)	0.004(3)
C(24)	2*i*		1.0188(6)	0.7352(4)	0.4031(3)	0.062(3)	0.053(3)	0.038(3)	0.023(3)	0.012(2)	0.010(2)
C(25)	2*i*		1.0898(6)	0.6645(5)	0.4449(3)	0.079(4)	0.079(4)	0.042(3)	0.036(3)	0.014(3)	0.022(3)
C(26)	2*i*		1.1358(6)	0.5899(5)	0.4028(3)	0.064(4)	0.073(3)	0.054(3)	0.031(3)	0.005(3)	0.028(3)
C(27)	2*i*		1.1179(5)	0.5772(4)	0.3155(3)	0.041(3)	0.048(3)	0.054(3)	0.017(2)	0.009(2)	0.020(2)
C(28)	2*i*		1.1637(6)	0.5028(4)	0.2689(3)	0.052(3)	0.052(3)	0.072(4)	0.026(3)	0.017(3)	0.024(3)
C(29)	2*i*		1.1415(5)	0.4974(4)	0.1865(3)	0.047(3)	0.045(3)	0.071(3)	0.022(2)	0.016(3)	0.006(3)
C(30)	2*i*		1.0690(5)	0.5653(4)	0.1484(3)	0.041(3)	0.048(3)	0.049(3)	0.016(2)	0.016(2)	0.011(2)
C(31)	2*i*		1.0479(5)	0.6445(3)	0.2734(2)	0.029(3)	0.036(2)	0.041(3)	0.004(2)	0.008(2)	0.012(2)
C(32)	2*i*		0.9990(5)	0.7241(3)	0.3181(2)	0.039(3)	0.034(2)	0.038(2)	0.010(2)	0.010(2)	0.009(2)
C(33)	2*i*	0.5	0.474(1)	0.9109(9)	0.3948(6)	0.093(9)	0.072(7)	0.060(7)	0.052(7)	0.020(6)	0.026(6)
C(34)	2*i*		0.596(1)	0.7633(7)	0.6114(5)	0.129(8)	0.139(7)	0.116(6)	0.062(6)	0.023(5)	0.002(5)
S(1)	2*i*		0.7445(1)	0.61346(9)	0.02696(7)	0.0579(8)	0.0331(6)	0.0403(6)	0.0099(5)	0.0055(6)	0.0137(5)
N(1)	2*i*		0.7161(4)	0.3890(3)	–0.0205(2)	0.050(3)	0.042(2)	0.048(2)	0.015(2)	0.019(2)	0.011(2)
N(2)	2*i*		0.6782(5)	0.2881(3)	0.0075(2)	0.072(3)	0.043(2)	0.056(3)	0.026(2)	0.021(2)	0.008(2)
N(3)	2*i*		0.6495(4)	0.3034(3)	0.0774(2)	0.060(3)	0.029(2)	0.055(2)	0.014(2)	0.014(2)	0.010(2)
N(4)	2*i*		0.6682(4)	0.4185(3)	0.0968(2)	0.037(2)	0.032(2)	0.043(2)	0.010(2)	0.011(2)	0.010(2)
N(5)	2*i*		1.1493(4)	0.8793(3)	0.1551(2)	0.035(2)	0.042(2)	0.047(2)	0.006(2)	0.010(2)	0.014(2)
N(6)	2*i*		0.8535(4)	0.8687(3)	0.1114(2)	0.042(2)	0.034(2)	0.039(2)	0.014(2)	0.012(2)	0.011(2)
N(7)	2*i*		0.9304(4)	0.7855(3)	0.2724(2)	0.050(2)	0.035(2)	0.038(2)	0.017(2)	0.009(2)	0.008(2)
N(8)	2*i*		1.0221(4)	0.6369(3)	0.1906(2)	0.034(2)	0.034(2)	0.040(2)	0.009(2)	0.013(2)	0.009(2)
O(1)	2*i*		0.6683(4)	0.5658(3)	0.4690(2)	0.091(3)	0.097(3)	0.044(2)	0.049(2)	0.022(2)	0.020(2)
O(2)	2*i*		0.5245(5)	0.6567(4)	0.4100(2)	0.104(3)	0.118(3)	0.064(2)	0.073(3)	0.031(2)	0.022(2)
O(3)	2*i*		0.9681(7)	0.2968(4)	0.3611(3)	0.195(6)	0.087(3)	0.089(3)	0.023(4)	0.042(3)	–0.013(3)
O(4)	2*i*		0.8237(8)	0.1981(5)	0.2319(3)	0.227(7)	0.201(6)	0.068(3)	0.151(6)	0.009(3)	0.012(3)
O(5)	2*i*		0.8040(9)	0.1040(5)	0.3372(5)	0.188(7)	0.128(5)	0.248(8)	0.024(5)	0.060(6)	0.097(5)
O(6)	2*i*		1.0198(7)	0.1475(5)	0.3006(4)	0.110(5)	0.142(5)	0.254(8)	0.071(4)	0.005(5)	0.019(5)
O(7)	2*i*	0.5	0.469(1)	0.8277(6)	0.3355(4)	0.132(7)	0.061(4)	0.047(4)	0.057(5)	0.010(4)	0.023(4)
O(8)	2*i*		0.6739(6)	0.6838(4)	0.6118(3)	0.094(4)	0.115(3)	0.074(3)	0.033(3)	0.021(3)	0.006(3)
Cl(1)	2*i*		0.8970(2)	0.1875(1)	0.30720(8)	0.080(1)	0.0570(8)	0.0564(8)	0.0221(8)	0.0016(7)	0.0086(7)

References

1. Li, Y.; Xu, G.; Zou, W.-Q.; Wang, M.-S.; Zheng, F.-K.; Wu, M.-F.; Zeng, H.-Y.; Guo, G.-C.; Huang. J.-S.: A novel metal-organic network with high thermal stability: nonlinear optical and photoluminescent properties. Inorg. Chem. **47** (2008) 7945-947.
2. Rodríuez-Diéguez, A.; Salinas-Castillo, A.; Galli, S.; Masciocchi, N.; Gutiérrez-Zorrilla, J. M.; Vitoria, P.; Colacio, E.: Synthesis, X-ray structures and luminescence properties of three multidimensional metal-organic frameworks incorporating the versatile 5-(pyrimidyl) tetrazolato bridging ligand. Dalton Trans. (2007) 1821-1827.
3. He, X.; Lu, C. Z.; Wu, C. D.; Chen, L. J.: A Series of One- to Three-Dimensional Copper Coordination Polymers Based on N-Heterocyclic Ligands. Eur. J. Inorg. Chem. (2006) 2491-2503.
4. Zhang, X. M.; Hao, Z. M.; Zhang, W. X.; Chen, X. M.: Dehydration-Induced Conversion from a Single-Chain Magnet into a Metamagnet in a Homometallic Nanoporous Metal-Organic Framework. Angew. Chem. Int. Ed. **46** (2007) 3456-3459.
5. Liu, C.-S.; Sañudo, E. C.; Hua, M.; Zhang, Q.; Guo, L.-Q.; Fang, S.-M.: A cobalt(II) coordination polymer with mixed 4-(5-mercapto-1*H*-tetrazol-1-yl) benzoate and 4,4′-bipyridine ligands: synthesis, crystal structure, and magnetic properties. J. Coord. Chem. **63** (2010) 3393-3402.
6. Andrea, B.; Lippolis, V.: 1,10-Phenanthroline: A versatile building block for the construction of ligands for various purposes. Coord. Chem. Rev. **254** (2010) 2096–2180.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
8. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.