Crystal structure of bis(2,2′-bipyridine-*N*,*N*′)(*N*-tosyl-β-alaninato-*O*)-copper(II) chloride tetrahydrate, $[Cu(C_{10}H_8N_2)_2(C_{10}H_{12}NO_4S)]Cl \cdot 4H_2O$

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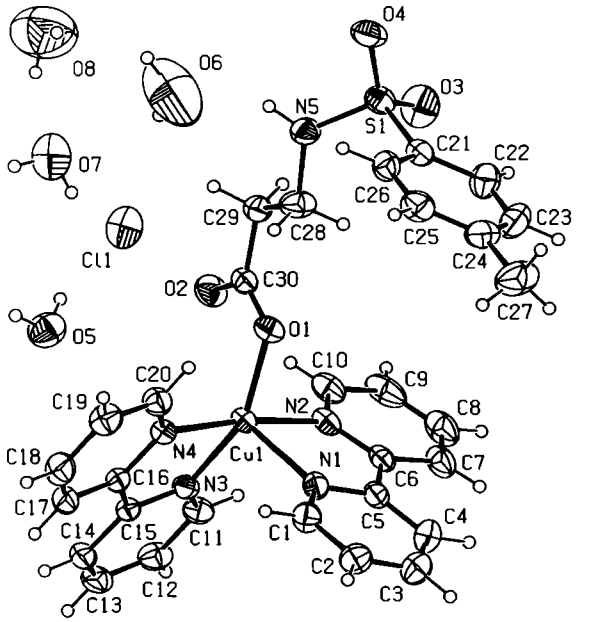

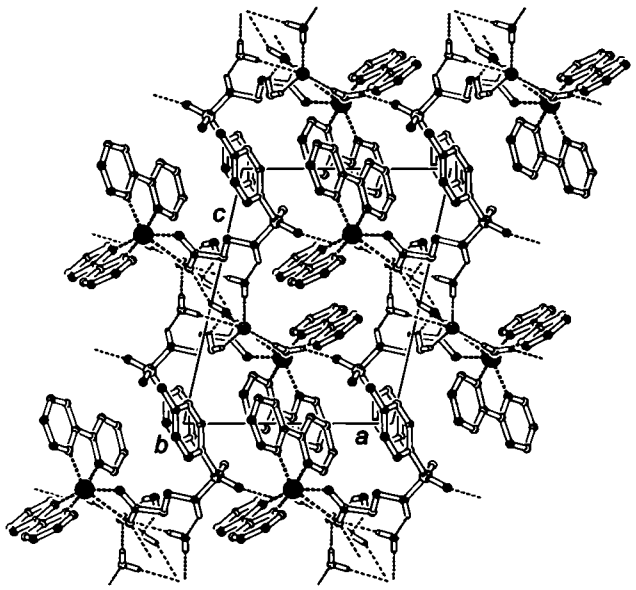

Abstract

$C_{30}H_{36}ClCuN_5O_8S$, triclinic, $P\bar{1}$ (no. 2), a = 10.428(2) Å, b = 12.785(2) Å, c = 13.838(2) Å, α = 68.583(2)°, β = 73.664(2)°, γ = 77.367(2)°, V = 1634.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.153, T = 293 K.

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Source of material

The mixture of $CuCl_2 \cdot 2H_2O$ (1 mmol) and *N*-*p*-tolysulfonyl-β-alanine (2 mmol) was stirred into 15 mL aqueous solution at room temperature. Then the pH was adjusted to approximately 6 with 1 M NaOH and 5 mL ethanol solution of 2,2′-bipyridine (1 mmol) was added. The reaction mixture was heated on a water bath, hold for 6 h at 70 °C, and then filtered. The blue crystal was separated from the mother liquor by slow evaporation at room temperature after 4 weeks (yield 0.38 g, 56 %).

Experimental details

Due to the disorder of the O6, O7 and O8 atoms, only two of the eight water hydrogen atoms could be found from Fourier difference maps. The six remaining H atoms were added according to the donor-acceptor concept under consideration of appropriate Cl···O and O···O distances (d(Cl···O) ≈ 3.2 Å and d(O···O) ≈ 2.9 Å and restrained bond parameters (d(O—H) = 0.82 Å, ∠H–O–H = 110°).

Discussion

As the essential trace element in organisms, copper similarly to other trace metallic elements exist in high-concentration bio-ligand environments, and often form mixed-ligand complexes with more than two ligands. Such complexes play a very important role in enzyme catalyzing, storage and conveyance of substance as well as in transporting metallic ions during the life process. Therefore, study on mixed-ligand complexes of metal ions with bio-ligands will be of great importance towards exploring mechanism of functional activity of microelements in organisms. N-protected amino acids, being biologically important compounds derived from naturally occurring amino acids, have been studied extensively in the coordination chemistry of metal ions [1-8]. In the present investigation, a ternary complex of copper(II) ion with *N*-*p*-tolysulfonyl-β-alanine (H-ts-β-ala), as primary ligand and 2,2′-bipyridine as secondary ligand, has been characterized.

The asymmetric unit of the crystal structure consists of a discrete $[Cu(bipy)_2(ts\text{-}\beta\text{-}ala)]^+$ cation, a counter chloride anion and four hydrate water molecules (figure, top). The co-ordinated ts-β-ala monoanion acts as a monodentate ligand. The Cu ion is five-coordinated (CuN_4O) and the coordination polyhedron can be described as an distorted square pyramid. The equatorial plane is formed by N1, N2, N3 and N4 from two bipy molecules. The bond lengths of Cu1—N1, Cu1—N2, Cu1—N3 and Cu1—N4 are 2.194(3) Å, 2.017(3) Å, 2.053(3) Å and 1.997(3) Å, respectively. The axial position is occupied by the O atom from the *N*-*p*-tolylsulfonyl-β-alanine ligand. The distance of the axial Cu1—O1 is 1.987(2) Å. The Cu—O and Cu—N bond lengths are close to those found in copper(II) complexes of N-protected amino acids and 2,2′-bipyridine [9-10]. Both of the non-coordinated Cl^- an-

ions and water molecules fill the space between cations (figure, bottom). It is noteworthy that hydrogen bond interactions play an important role. Several kinds of hydrogen bonding are observed in the crystal structure: (a) hydrogen bonding between water oxygen atoms and nitrogen atoms of sulfonamide groups (N5–H5N···O5 with the bond distance of 2.891(5) Å and bond angle of 128°), (b) hydrogen bonding between water oxygen atoms and uncoordinated chloride anion (O5–H5OA···Cl1 and O5–H5OB···Cl1 with the bond distances of 3.165(4) Å and 3.185(4) Å and bond angles of 169° and 170°, respectively). At the same time, several weak C–H···O hydrogen bonds are formed, in which carboxylate O and sulfonamide O atoms have interactions with H atoms from 2,2′-bipyridine group and benzene ring. Moreover, there are aromatic ring stacking interactions between bipyridine and benzene rings. The centroid distance between the 2,2′-bipyridine molecule and benzene ring is 3.79 Å. These weak π-π stacking interactions and the weak hydrogen bonds form a complex 2D supramolecular network forming by self-assembly and stabilizing the supramolecular structure.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.20 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.71 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8861, 5958
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5182
$N(param)_{refined}$:	416
Programs:	SHELXS-97 [11], SHELXL-97 [12]

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

Atom	Site	x	y	z	U_{iso}
H(5N)	2*i*	1.1780	0.4888	0.6361	0.069
H(1)	2*i*	0.3872	0.6107	0.8574	0.067
H(2)	2*i*	0.2656	0.5265	1.0244	0.079
H(3)	2*i*	0.2808	0.5753	1.1648	0.090
H(4)	2*i*	0.4213	0.7072	1.1347	0.084
H(7)	2*i*	0.5605	0.8286	1.0946	0.080
H(8)	2*i*	0.6992	0.9666	1.0406	0.095
H(9)	2*i*	0.8023	1.0375	0.8626	0.095
H(10)	2*i*	0.7632	0.9683	0.7418	0.076
H(11)	2*i*	0.4916	1.0533	0.7376	0.061
H(12)	2*i*	0.3383	1.1964	0.6636	0.072
H(13)	2*i*	0.2172	1.1683	0.5607	0.074
H(14)	2*i*	0.2554	0.9947	0.5332	0.066
H(17)	2*i*	0.2928	0.8192	0.5254	0.068
H(18)	2*i*	0.3597	0.6383	0.5125	0.079
H(19)	2*i*	0.5377	0.5266	0.5845	0.077
H(20)	2*i*	0.6437	0.5947	0.6694	0.065
H(22)	2*i*	1.1174	0.3794	1.0156	0.084
H(23)	2*i*	0.9796	0.2538	1.1449	0.095
H(25)	2*i*	0.9424	0.1319	0.9299	0.080
H(26)	2*i*	1.0787	0.2559	0.7990	0.069
H(27A)	2*i*	0.7876	0.0860	1.1105	0.155
H(27B)	2*i*	0.8140	0.1273	1.1960	0.155
H(27C)	2*i*	0.9089	0.0255	1.1654	0.155
H(28A)	2*i*	0.9387	0.5209	0.7129	0.080
H(28B)	2*i*	0.9829	0.5533	0.7968	0.080
H(29A)	2*i*	1.0317	0.6757	0.5790	0.062
H(29B)	2*i*	1.0688	0.7091	0.6650	0.062
H(5A)	2*i*	0.1506	0.4349	0.5008	0.126
H(5B)	2*i*	0.0545	0.3726	0.5715	0.126
H(6A)	2*i*	1.0009	0.0884	0.5311	0.394
H(6B)	2*i*	0.8990	0.0245	0.5799	0.394
H(7A)	2*i*	0.6460	0.2645	0.6932	0.180
H(7B)	2*i*	0.5156	0.2538	0.7069	0.180
H(8A)	2*i*	0.9768	0.1325	0.6503	0.360
H(8B)	2*i*	0.9003	0.2028	0.7033	0.360

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*	0.59810(4)	0.80108(3)	0.74205(3)	0.0384(2)	0.0421(2)	0.0473(2)	−0.0018(2)	−0.0165(2)	−0.0147(2)
S(1)	2*i*	1.22070(9)	0.42327(8)	0.79266(8)	0.0494(5)	0.0542(5)	0.0662(6)	−0.0094(4)	−0.0177(4)	−0.0189(4)
O(1)	2*i*	0.7705(2)	0.6973(2)	0.7377(2)	0.044(1)	0.051(1)	0.064(2)	0.001(1)	−0.018(1)	−0.016(1)
O(2)	2*i*	0.8536(3)	0.8467(2)	0.6110(2)	0.066(2)	0.054(2)	0.069(2)	−0.002(1)	−0.022(1)	−0.006(1)
O(3)	2*i*	1.2386(4)	0.5020(3)	0.8371(3)	0.113(3)	0.092(2)	0.099(2)	−0.053(2)	−0.022(2)	−0.037(2)
O(4)	2*i*	1.3365(3)	0.3575(3)	0.7480(2)	0.045(1)	0.075(2)	0.085(2)	0.003(1)	−0.014(1)	−0.015(2)
N(1)	2*i*	0.4757(3)	0.7071(2)	0.8941(2)	0.049(2)	0.050(2)	0.044(1)	−0.005(1)	−0.016(1)	−0.015(1)
N(2)	2*i*	0.6388(3)	0.8624(2)	0.8438(2)	0.045(2)	0.047(2)	0.064(2)	−0.001(1)	−0.026(1)	−0.020(1)
N(3)	2*i*	0.4675(3)	0.9400(2)	0.6811(2)	0.037(1)	0.043(1)	0.045(1)	−0.004(1)	−0.009(1)	−0.010(1)
N(4)	2*i*	0.5330(3)	0.7434(2)	0.6506(2)	0.040(1)	0.047(2)	0.042(1)	−0.003(1)	−0.010(1)	−0.014(1)
N(5)	2*i*	1.1422(3)	0.4903(3)	0.6998(2)	0.051(2)	0.054(2)	0.056(2)	0.004(1)	−0.009(1)	−0.014(1)
C(1)	2*i*	0.3943(4)	0.6305(3)	0.9139(3)	0.057(2)	0.058(2)	0.054(2)	−0.018(2)	−0.013(2)	−0.016(2)
C(2)	2*i*	0.3208(4)	0.5797(4)	1.0137(3)	0.058(2)	0.071(3)	0.061(2)	−0.020(2)	−0.007(2)	−0.011(2)
C(3)	2*i*	0.3302(5)	0.6082(4)	1.0966(3)	0.070(3)	0.092(3)	0.051(2)	−0.020(2)	−0.004(2)	−0.010(2)
C(4)	2*i*	0.4137(5)	0.6868(4)	1.0787(3)	0.076(3)	0.091(3)	0.048(2)	−0.008(2)	−0.015(2)	−0.027(2)
C(5)	2*i*	0.4859(3)	0.7348(3)	0.9765(3)	0.046(2)	0.052(2)	0.049(2)	0.003(1)	−0.020(1)	−0.018(2)
C(6)	2*i*	0.5780(3)	0.8212(3)	0.9477(3)	0.047(2)	0.051(2)	0.058(2)	0.011(1)	−0.028(2)	−0.025(2)
C(7)	2*i*	0.6011(4)	0.8586(4)	1.0230(4)	0.070(3)	0.076(3)	0.075(3)	0.008(2)	−0.038(2)	−0.042(2)
C(8)	2*i*	0.6843(5)	0.9399(4)	0.9910(5)	0.079(3)	0.088(3)	0.104(4)	0.007(3)	−0.049(3)	−0.058(3)
C(9)	2*i*	0.7455(5)	0.9822(4)	0.8854(5)	0.060(2)	0.072(3)	0.136(5)	−0.003(2)	−0.048(3)	−0.053(3)
C(10)	2*i*	0.7211(4)	0.9407(3)	0.8133(4)	0.054(2)	0.063(2)	0.087(3)	−0.008(2)	−0.031(2)	−0.028(2)
C(11)	2*i*	0.4438(4)	1.0412(3)	0.6959(3)	0.047(2)	0.044(2)	0.061(2)	−0.003(1)	−0.012(2)	−0.017(2)
C(12)	2*i*	0.3519(4)	1.1273(3)	0.6520(3)	0.056(2)	0.043(2)	0.069(2)	0.000(2)	−0.004(2)	−0.014(2)
C(13)	2*i*	0.2802(4)	1.1108(3)	0.5908(3)	0.049(2)	0.056(2)	0.061(2)	0.007(2)	−0.014(2)	−0.003(2)
C(14)	2*i*	0.3029(4)	1.0077(3)	0.5746(3)	0.044(2)	0.065(2)	0.047(2)	−0.003(2)	−0.015(2)	−0.006(2)
C(15)	2*i*	0.3971(3)	0.9232(3)	0.6206(2)	0.034(2)	0.049(2)	0.036(2)	−0.006(1)	−0.007(1)	−0.009(1)
C(16)	2*i*	0.4307(3)	0.8101(3)	0.6074(2)	0.037(2)	0.053(2)	0.036(2)	−0.009(1)	−0.006(1)	−0.011(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(17)	2*i*	0.3637(4)	0.7726(4)	0.5548(3)	0.048(2)	0.076(2)	0.051(2)	−0.014(2)	−0.015(2)	−0.020(2)
C(18)	2*i*	0.4037(4)	0.6652(4)	0.5468(3)	0.067(3)	0.081(3)	0.065(2)	−0.025(2)	−0.015(2)	−0.034(2)
C(19)	2*i*	0.5089(4)	0.5989(4)	0.5897(3)	0.070(3)	0.062(2)	0.069(2)	−0.014(2)	−0.011(2)	−0.032(2)
C(20)	2*i*	0.5718(4)	0.6401(3)	0.6408(3)	0.055(2)	0.053(2)	0.058(2)	−0.001(2)	−0.016(2)	−0.022(2)
C(21)	2*i*	1.1135(3)	0.3294(3)	0.8937(3)	0.046(2)	0.051(2)	0.056(2)	−0.001(1)	−0.018(2)	−0.019(2)
C(22)	2*i*	1.0828(5)	0.3294(4)	0.9978(3)	0.085(3)	0.072(3)	0.064(2)	−0.010(2)	−0.018(2)	−0.035(2)
C(23)	2*i*	0.9998(5)	0.2539(4)	1.0750(3)	0.091(3)	0.087(3)	0.053(2)	−0.006(3)	−0.003(2)	−0.027(2)
C(24)	2*i*	0.9463(4)	0.1789(4)	1.0518(4)	0.053(2)	0.064(2)	0.071(3)	−0.004(2)	−0.004(2)	−0.015(2)
C(25)	2*i*	0.9777(4)	0.1816(4)	0.9476(4)	0.059(2)	0.067(2)	0.077(3)	−0.020(2)	−0.016(2)	−0.020(2)
C(26)	2*i*	1.0596(4)	0.2556(3)	0.8689(3)	0.059(2)	0.064(2)	0.055(2)	−0.012(2)	−0.017(2)	−0.023(2)
C(27)	2*i*	0.8559(6)	0.0969(5)	1.1390(4)	0.085(4)	0.096(4)	0.095(4)	−0.022(3)	0.013(3)	−0.009(3)
C(28)	2*i*	1.0056(4)	0.5556(3)	0.7231(4)	0.052(2)	0.052(2)	0.076(3)	−0.000(2)	−0.004(2)	−0.012(2)
C(29)	2*i*	1.0035(3)	0.6748(3)	0.6524(3)	0.046(2)	0.054(2)	0.052(2)	−0.003(2)	−0.011(2)	−0.013(2)
C(30)	2*i*	0.8671(3)	0.7467(3)	0.6668(3)	0.043(2)	0.051(2)	0.051(2)	−0.004(1)	−0.017(1)	−0.017(2)
Cl(1)	2*i*	0.8161(1)	0.3853(1)	0.6264(1)	0.0752(7)	0.113(1)	0.0790(7)	−0.0204(7)	−0.0058(6)	−0.0402(7)
O(5)	2*i*	0.1351(3)	0.3790(3)	0.5535(3)	0.073(2)	0.090(2)	0.088(2)	0.004(2)	−0.019(2)	−0.034(2)
O(6)	2*i*	0.9221(7)	0.0871(7)	0.5639(6)	0.142(6)	0.30(1)	0.218(8)	−0.102(6)	−0.045(5)	0.109(7)
O(7)	2*i*	0.5899(5)	0.2203(4)	0.7165(4)	0.120(3)	0.127(4)	0.126(3)	−0.027(3)	−0.030(3)	−0.049(3)
O(8)	2*i*	0.9453(9)	0.1405(7)	0.7089(8)	0.214(8)	0.188(7)	0.244(9)	−0.019(6)	−0.036(7)	0.001(6)

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