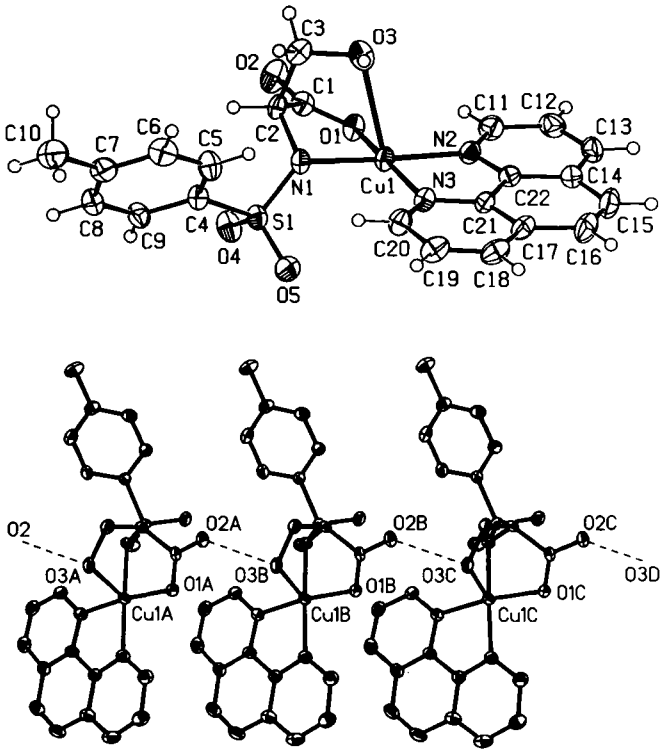
Crystal structure of (1,10-phenanthroline)(*N*-tosyl-serinato)copper(II), $Cu(C_{12}H_8N_2)(C_{10}H_{11}NO_5S)$

J.-G. Wang, L.-F. Ma, L.-Y. Wang*, Y.-H. Wang and R. Liu

Luoyang Normal University, Department of Chemistry, Luoyang, Henan, 471022 P. R. China

Received October 15, 2005, accepted and available on-line December 4, 2005; CCDC no. 1267/1663



Abstract

$C_{22}H_{19}CuN_3O_5S$, triclinic, $P\bar{1}$ (no. 1), $a = 6.2202(7)$ Å, $b = 9.416(1)$ Å, $c = 10.339(2)$ Å, $\alpha = 109.186(2)°$, $\beta = 105.136(2)°$, $\gamma = 103.455(2)°$, $V = 517.3$ Å^3, $Z = 1$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.059$, $T = 296$ K.

Source of material

The mixture of $Cu(CH_3COO)_2 \cdot 6H_2O$ (1 mmol), 1,10-phenanthroline hydrate (1 mmol) and *N*-*p*-tolylsulfonyl-serine (ts-serH_2; 2 mmol) was stirred into an aqueous solution (12 mL) about ten minutes to obtain a blue solution which was refluxed about 30 minutes. Then the pH was adjusted to 8 with 2 M NaOH solution. The reaction mixture was heated on a water bath for 10 h at 70 °C, and then filtered. The blue crystal was separated from the mother liquor by slow evaporation at room temperature after nine days.

Experimental details

Except the hydroxyl H atom which was refined freely, the H atoms were fixed at calculated positions and treated in riding rigid body approximation.

* Correspondence author (e-mail: wlya@lynu.edu.cn)

Discussion

Interactions of biologically active metal ions such as copper(II) with amino acids and peptide derivatives are of considerable interest as these often represent the role of metal ions in enzymes [1-5]. Sulfonamides derived from amino acids and peptides offer two or more potential binding sites for metal ions. Benzenesulfonamide has been shown to be the most potent amongst the sulfonamides in the selective inhibition of animal and bacterial carbonic anhydrases [6-10]. That this inhibitory action is at least partially due to the ionization of the sulfonamide molecule by deprotonation at the amido nitrogen, upon coordination to the metalloenzyme, has been shown from crystallographic and spectroscopic studies. The ligand *N*-*p*-tolylsulfonyl-serine (*N*-tosyl-serine), which can be viewed either as a N-substituted sulfonamide or as a N-substituted amino acid, was expected to undergo deprotonation at the acidic sulfonamide nitrogen coordinated to a metal ion, resulting in a deprotonated amino nitrogen in the serine moiety. This would then be reminiscent of a deprotonated peptide nitrogen in a metal-peptide complex. At the same time, the study of ternary complexes involving an aromatic amine as the primary ligand, a metal ion and biomolecules as secondary ligands can provide useful models for gaining a better understanding of enzyme-metal ion-substrate complexes, which play an important role in metalloenzyme-catalysed biochemicals reactions. In the present investigation, a ternary complex of copper(II) ion with 1,10-phenanthroline as primary ligand and *N*-*p*-tolylsulfonyl-serine as secondary ligand, has been obtained.

The crystal structure of the title complex consists of discrete [Cu(phen)(ts-ser)] units (figure, top). The coordinated ts-ser dianion acts as a bidentate chelate ligand: The sulfonamide nitrogen, the carboxylate and the hydroxyl groups participate in coordination. The metal environment is formed by the two phen nitrogen, two oxygen atoms and one sulfonamide nitrogen atom from the ts-ser ligand, forming a distorted square-pyramidal arrangement, with Cu—O and Cu—N bond lengths being in the ranges 1.956(3) Å – 2.503(3) Å and 1.959(3) Å – 2.010(3) Å, respectively, which are close to those found in copper(II) complexes of N-protected amino acids [11]. The equatorial plane is formed by O1, N1, N2 and N3 atoms from ts-ser and 1,10-phenanthroline. The hydroxyl oxygen atom of the amino acid is in axial position, the distance between the hydroxyl oxygen atom and the copper ion is 2.503(3) Å, which is much longer than the distance between the coordinated carboxylate oxygen atom and the copper ion (1.956(3) Å). It is noteworthy that there are significant intermolecular contacts exiting between the complexes. The shortest contact distance of 2.645(4) Å is between the hydroxyl oxygen atoms and the carboxylate atoms, O3A···O2B, belonging to different ts-ser ligands. The crystal structure of the title complex can be characterized as one-dimensional chains formed by the intermolecular interactions (figure, bottom).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.18 × 0.18 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.98 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2756, 2258
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2224
$N(param)_{refined}$:	294
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(3)	1*a*	0.866(8)	0.663(5)	0.158(4)	0.04(1)
H(2)	1*a*	0.5756	0.6995	0.4132	0.036
H(3A)	1*a*	0.7120	0.8519	0.2848	0.044
H(3B)	1*a*	0.9050	0.7901	0.3561	0.044
H(5)	1*a*	1.0519	0.5946	0.4859	0.049
H(6)	1*a*	1.3534	0.7525	0.7125	0.051
H(8)	1*a*	0.8988	0.6784	0.9147	0.050
H(9)	1*a*	0.5938	0.5257	0.6896	0.045
H(10A)	1*a*	1.4754	0.7864	0.9996	0.084
H(10B)	1*a*	1.2992	0.8533	1.0634	0.084
H(10C)	1*a*	1.4358	0.9408	0.9877	0.084
H(11)	1*a*	0.1057	0.3927	−0.2009	0.048
H(12)	1*a*	−0.0074	0.2762	−0.4540	0.052
H(13)	1*a*	0.1766	0.1082	−0.5592	0.055
H(15)	1*a*	0.4880	−0.0280	−0.5209	0.059
H(16)	1*a*	0.7807	−0.0618	−0.3611	0.059
H(18)	1*a*	1.0305	0.0037	−0.0933	0.053
H(19)	1*a*	1.1100	0.1381	0.1517	0.051
H(20)	1*a*	0.9018	0.3036	0.2285	0.046

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*a*	0.48626(2)	0.39516(2)	0.06843(2)	0.0303(2)	0.0336(2)	0.0237(2)	0.0151(1)	0.0104(1)	0.0078(1)
S(1)	1*a*	0.5579(1)	0.41681(9)	0.39108(8)	0.0296(4)	0.0384(4)	0.0265(4)	0.0093(3)	0.0094(3)	0.0119(3)
O(1)	1*a*	0.2452(4)	0.4950(3)	0.0810(3)	0.027(1)	0.040(1)	0.031(1)	0.015(1)	0.009(1)	0.009(1)
O(2)	1*a*	0.2089(4)	0.7070(3)	0.2397(3)	0.033(1)	0.055(1)	0.052(2)	0.023(1)	0.017(1)	0.008(1)
O(3)	1*a*	0.7547(5)	0.6739(3)	0.1401(3)	0.027(1)	0.060(2)	0.040(1)	0.019(1)	0.015(1)	0.024(1)
O(4)	1*a*	0.3397(4)	0.4192(3)	0.4150(3)	0.026(1)	0.064(2)	0.039(1)	0.009(1)	0.012(1)	0.020(1)
O(5)	1*a*	0.5848(5)	0.2621(3)	0.3430(3)	0.060(2)	0.038(1)	0.040(1)	0.018(1)	0.015(1)	0.015(1)
N(1)	1*a*	0.6098(5)	0.4957(3)	0.2842(3)	0.034(2)	0.036(2)	0.023(2)	0.016(1)	0.011(1)	0.010(1)
N(2)	1*a*	0.3530(6)	0.3026(3)	−0.1530(3)	0.035(2)	0.029(1)	0.030(2)	0.014(1)	0.012(1)	0.010(1)
N(3)	1*a*	0.6928(5)	0.2628(3)	0.0318(3)	0.035(2)	0.032(1)	0.031(2)	0.012(1)	0.012(1)	0.008(1)
C(1)	1*a*	0.3177(6)	0.6141(4)	0.2039(4)	0.024(2)	0.038(2)	0.037(2)	0.014(1)	0.017(1)	0.016(1)
C(2)	1*a*	0.5646(5)	0.6484(3)	0.3113(3)	0.032(2)	0.031(1)	0.025(2)	0.016(1)	0.011(1)	0.005(1)
C(3)	1*a*	0.7497(6)	0.7566(4)	0.2810(4)	0.027(2)	0.034(1)	0.041(2)	0.011(1)	0.009(1)	0.009(1)
C(4)	1*a*	0.7910(6)	0.5432(4)	0.5643(4)	0.029(2)	0.037(2)	0.028(2)	0.013(1)	0.010(1)	0.011(1)
C(5)	1*a*	1.0201(6)	0.6120(4)	0.5717(4)	0.032(2)	0.056(2)	0.038(2)	0.018(2)	0.017(2)	0.018(2)
C(6)	1*a*	1.2006(6)	0.7067(4)	0.7081(4)	0.027(2)	0.050(2)	0.049(2)	0.012(1)	0.009(2)	0.022(2)
C(7)	1*a*	1.1585(6)	0.7346(4)	0.8380(4)	0.039(2)	0.038(2)	0.037(2)	0.014(1)	0.002(2)	0.017(1)
C(8)	1*a*	0.9296(7)	0.6633(4)	0.8288(4)	0.049(2)	0.047(2)	0.030(2)	0.016(2)	0.015(2)	0.017(1)
C(9)	1*a*	0.7468(6)	0.5703(4)	0.6938(4)	0.036(2)	0.045(2)	0.033(2)	0.010(1)	0.016(2)	0.018(2)
C(10)	1*a*	1.3609(8)	0.8384(5)	0.9858(4)	0.050(2)	0.051(2)	0.046(2)	0.008(2)	−0.005(2)	0.018(2)
C(11)	1*a*	0.1818(6)	0.3264(4)	−0.2421(4)	0.042(2)	0.039(2)	0.039(2)	0.017(1)	0.012(2)	0.016(1)
C(12)	1*a*	0.1118(7)	0.2559(4)	−0.3949(4)	0.047(2)	0.043(2)	0.038(2)	0.014(2)	0.007(2)	0.022(2)
C(13)	1*a*	0.2213(7)	0.1560(4)	−0.4574(4)	0.053(2)	0.042(2)	0.027(2)	0.001(2)	0.009(2)	0.012(1)
C(14)	1*a*	0.4011(7)	0.1267(4)	−0.3665(4)	0.047(2)	0.032(2)	0.031(2)	0.008(1)	0.017(2)	0.011(1)
C(15)	1*a*	0.5264(8)	0.0247(4)	−0.4200(4)	0.060(2)	0.046(2)	0.034(2)	0.016(2)	0.023(2)	0.003(2)
C(16)	1*a*	0.7012(7)	0.0045(4)	−0.3243(4)	0.053(2)	0.044(2)	0.046(2)	0.021(2)	0.026(2)	0.006(2)
C(17)	1*a*	0.7651(6)	0.0828(4)	−0.1688(4)	0.036(2)	0.028(1)	0.041(2)	0.011(1)	0.017(2)	0.006(1)
C(18)	1*a*	0.9448(7)	0.0683(4)	−0.0631(4)	0.039(2)	0.034(2)	0.059(2)	0.019(1)	0.020(2)	0.014(2)
C(19)	1*a*	0.9925(6)	0.1485(4)	0.0822(4)	0.033(2)	0.037(2)	0.051(2)	0.016(1)	0.008(2)	0.014(2)
C(20)	1*a*	0.8651(6)	0.2475(4)	0.1283(4)	0.034(2)	0.039(2)	0.034(2)	0.013(1)	0.008(1)	0.011(1)
C(21)	1*a*	0.6460(6)	0.1822(4)	−0.1138(4)	0.034(2)	0.025(1)	0.027(2)	0.007(1)	0.012(1)	0.006(1)
C(22)	1*a*	0.4604(6)	0.2044(4)	−0.2148(3)	0.032(2)	0.028(1)	0.030(2)	0.007(1)	0.011(1)	0.011(1)

Acknowledgments. This work was supported by the National Natural Science Foundation of China (grant no. 20471026), the Natural Science Foundation of Henan province (grant no. 311021200) and the Foundation of the Education Committee of Henan province (grant no. 2006150017).

References

1. Laura, E. G.; William, T. A. H.: Amino Acid Templating of Inorganic Networks: Synthesis and Structure of L-Asparagine Zinc Phosphite, $(C_4N_2O_3H_8)ZnHPO_3$. Inorg. Chem. **43** (2004) 1808-1809.
2. Mandal, H. S.; Kraatz, H. B.: Ferrocene-Histidine Conjugates: *N*-Ferrocenoyl-histidyl(im*N*-ferrocenoyl)methyl ester: Synthesis and Structure. J. Organomet. Chem. **674** (2003) 32-37.
3. Zhang, J.-J.; Sheng, T.-L.; Hu, S.-M.; Xia, S.-Q.; Leibeling, G.; Meyer, F.; Fu, Z.-Y.; Chen, L.; Fu, R.-B.; Wu, X.-T.: Two 3D Supramolecular Polymers Constructed from an Amino Acid and a High-Nuclear Ln_6Cu_{24} Cluster Node. Chem. Eur. J. **10** (2004) 3963-3969.
4. Zhang, J.-J.; Xia, S.-Q.; Sheng, T.-L.; Hu, S.-M.; Leibeling, G.; Meyer, F.; Wu, X.-T.; Xiang, S.-C.; Fu, R.-B.: A novel 2D net-like supramolecular polymer constructed from Ln_6Cu_{24} node and *trans*-$Cu(Gly)_2$ bridge. Chem. Commun. (2004) 1186-1187.

5. Ma, L.-F.; Wang, L.-Y.; Liang, F.-P.: Synthesis, characterization and crystal structure of holmium complex with β-alanine. Chin. J. Struct. Chem. **23** (2004) 207-212.
6. Ma, L.-F.; Yao, J.-C.; Wang, L.-Y.; Liang, F.-P.; Zhang, M.-B.: Synthesis and crystal structure of praseodymium complex with *N*-benzenesulfonyl-β-alanine. Chin. J. Struct. Chem. **23** (2004) 1056-1060.
7. Bonamartini, C. A.; Lusvardi, G.; Menabue, L.: Coordination properties of *N*-*p*-tolylsulfonyl-L-glutamic acid toward metal^{II}: Part 1. Crystallographic study on Zn^{II} and Cd^{II} complexes. Polyhedron **18** (1999) 1975-1982.
8. Battistuzzi, G.; Borsari, M.; Menabue, L.; Saladini, M.: Amide group coordination to the Pb^{2+} ion. Inorg. Chem. **35** (1996) 4239-4247.
9. Bonamartini Corradi, A.; Monabue, L.; Saladini, M.; Pietro Battaglia, M.: Deprotonated amide nitrogen co-ordination to the cadmium(II) ion in ternary 2,2′-bipyridine complexes with *N*-sulfonyl amino acids. J. Chem. Soc., Dalton Trans. (1992) 2623-2628.
10. Bonamartini Corradi, A.; Gozzoli, E.; Monabue, L.; Saladini, M.; Battaglia, L. P.; Sgarabtto, P.: Palladium(II) complexes of *N*-sulfonyl-amino acids. Part 1. Solid-state behaviour of binary and ternary 2,2′-bipyridine-containing systems. J. Chem. Soc., Dalton Trans. (1994) 273-278.
11. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
12. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.