Crystal structure of diaqua(1,10-phenanthroline)(*N*-tosylalaninato)-(formato)cobalt(II), $Co(H_2O)_2(C_{12}H_8N_2)(C_{10}H_{12}O_4NS)(CHO_2)$

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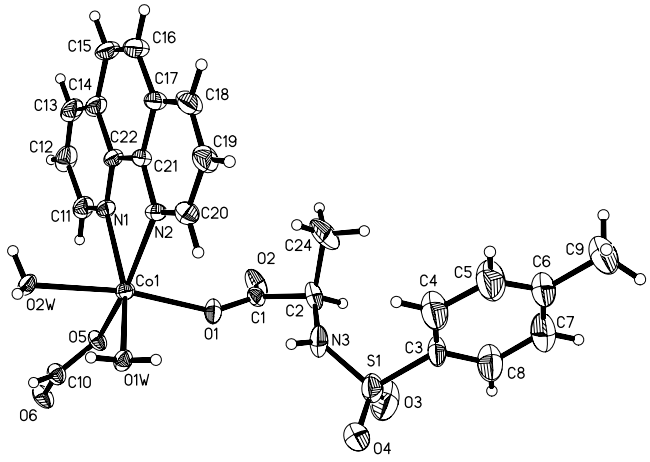

Abstract

$C_{23}H_{25}CoN_3O_8S$, monoclinic, $P12_1/c1$ (no. 14), a = 23.944(2) Å, b = 9.929(1) Å, c = 10.803(1) Å, β = 92.750(2)°, V = 2565.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.068, $wR_{ref}(F^2)$ = 0.221, T = 293 K.

Source of material

N-*p*-tolylsulfonylalanine (ts-alaH_2, 0.5 mmol, 0.116 g) and $Co(OAc)_2 \cdot 4H_2O$ (0.25 mmol, 0.064 g) were dissolved in 10 ml distilled water. And 5 mL DMF solution of 1,10-phenanthroline (phen, 0.25 mmol, 0.050 g) was added. Then the mixture was placed in a Teflon-lined stainless vessel (25 ml). The vessel was sealed, heated at 393 K for 72 h under autogenous pressure, and then cooled down to room temperature. The red block-shaped single crystals suitable for analysis were obtained from the resulting solution by filtering.

Experimental details

Hydrogen atoms bonded to carbon atoms were placed geometrically and treated as riding with d(C—H) = 0.93 Å, with U_{iso}(H) = 1.2 U_{eq}(C). The hydrogen atoms of water found in difference Fourier map were refined with restraints for d(O—H) = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(O). The large residual values are due to the large temperatural factors of C4 - C9 and O3.

Discussion

N-sulfonyl amino acids derived by substitution of an Ar-SO-group on the amine nitrogen of amino acids, have crystal structures analogous to the O-terminal of peptides [1,2]. Their coordination behaviour may show similar properties to the terminal-O of peptides and proteins. On the other hand, the ligand *N*-*p*-tolylsulfonylalanine (*N*-tosylalanine), 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 [3,4]. Moreover, 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 [5,6].
The crystal structure of the title complex consists of discrete $[Co(phen)(ts\text{-}ala)(HCOO)(H_2O)_2]$ units. The ts-ala anion acts as a monodentate ligand. The sulfonamide nitrogen does not participate in coordination. Instead, the formate formed through the decompose of DMF coordinates Co(II) ion. The metal environment is formed by the two phen nitrogens, two oxygen atoms from one ts-ala ligand and one formate, and another two O atoms from two water molecules, forming a distorted octahedral arrangement, with Co—O and Co—N bond lengths being in the ranges 2.104(3) - 2.238(3) Å and 2.278(3) - 2.301(4) Å, respectively. It is noteworthy that there is significant intermolecular hydrogen bonding interaction between the title complexes. The crystal structure can be viewed as two-dimensional layer formed by the intermolecular interactions.

Table 1. Data collection and handling.

Crystal:	red block, size 0.18 × 0.20 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.02 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14312, 5018
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3659
$N(param)_{refined}$:	327
Programs:	SHELXS-97, SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.3364	0.2501	0.1821	0.063
H(4)	4*e*	0.4010	0.2799	0.5178	0.114
H(5)	4*e*	0.4896	0.3624	0.5727	0.126
H(7)	4*e*	0.5571	0.1118	0.3452	0.121
H(8)	4*e*	0.4699	0.0152	0.2986	0.114
H(9A)	4*e*	0.5935	0.3919	0.4562	0.192
H(9B)	4*e*	0.6163	0.2473	0.4882	0.192
H(9C)	4*e*	0.5881	0.3331	0.5899	0.192
H(10)	4*e*	0.0334	0.1874	0.2944	0.047

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(11)	4*e*	0.0740	0.4891	0.0771	0.060
H(12)	4*e*	0.0474	0.6952	–0.0094	0.075
H(13)	4*e*	0.0816	0.8883	0.0750	0.076
H(15)	4*e*	0.1462	1.0083	0.2480	0.076
H(16)	4*e*	0.2095	0.9888	0.4036	0.077
H(18)	4*e*	0.2657	0.8425	0.5531	0.075
H(19)	4*e*	0.2826	0.6334	0.6324	0.072
H(20)	4*e*	0.2359	0.4513	0.5481	0.059

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(23A)	4*e*	0.3138	0.4632	0.3467	0.130
H(23B)	4*e*	0.3297	0.4854	0.2091	0.130
H(23C)	4*e*	0.3735	0.4236	0.3055	0.130
H(3)	4*e*	0.2954	0.2066	0.4103	0.074
H(1WB)	4*e*	0.1242	0.2606	0.5374	0.043
H(1WA)	4*e*	0.1791	0.2312	0.5124	0.043
H(2WB)	4*e*	0.0491	0.5053	0.3909	0.045
H(2WA)	4*e*	0.0608	0.4162	0.4885	0.045

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}
Co(1)	4*e*	0.14057(2)	0.37126(6)	0.32727(5)	0.0323(4)	0.0268(4)	0.0377(4)	0.0002(2)	–0.0014(2)	–0.0003(2)
C(1)	4*e*	0.2536(2)	0.2979(5)	0.1935(4)	0.028(2)	0.038(2)	0.048(3)	–0.008(2)	0.000(2)	–0.008(2)
C(2)	4*e*	0.3133(2)	0.2860(6)	0.2470(5)	0.026(2)	0.075(3)	0.056(3)	–0.008(2)	0.004(2)	–0.005(2)
C(3)	4*e*	0.4267(2)	0.1410(6)	0.3970(6)	0.027(2)	0.078(3)	0.076(3)	0.004(2)	–0.001(2)	–0.004(3)
C(4)	4*e*	0.4322(3)	0.2441(9)	0.4818(7)	0.056(3)	0.120(4)	0.109(4)	–0.006(3)	0.000(3)	–0.020(3)
C(5)	4*e*	0.4861(3)	0.295(1)	0.5133(9)	0.063(3)	0.128(4)	0.122(4)	–0.006(3)	–0.013(3)	–0.019(4)
C(6)	4*e*	0.5310(3)	0.2520(8)	0.4641(8)	0.045(3)	0.099(4)	0.121(4)	–0.002(3)	–0.007(3)	0.009(3)
C(7)	4*e*	0.5256(3)	0.146(1)	0.3813(9)	0.051(3)	0.132(4)	0.121(4)	0.005(3)	0.015(3)	0.000(4)
C(8)	4*e*	0.4727(3)	0.089(1)	0.3511(8)	0.056(3)	0.117(4)	0.112(4)	0.006(3)	0.010(3)	–0.014(4)
C(9)	4*e*	0.5874(3)	0.312(1)	0.503(1)	0.064(5)	0.126(7)	0.192(7)	–0.028(4)	–0.025(5)	0.027(6)
C(10)	4*e*	0.0458(2)	0.1872(5)	0.2141(4)	0.037(3)	0.045(3)	0.036(2)	–0.004(2)	0.009(2)	–0.006(2)
C(11)	4*e*	0.0878(2)	0.5681(6)	0.1132(5)	0.047(3)	0.050(3)	0.053(2)	0.012(2)	0.006(2)	0.017(2)
C(12)	4*e*	0.0719(3)	0.6923(6)	0.0600(5)	0.059(3)	0.068(3)	0.062(3)	0.024(3)	0.007(2)	0.030(2)
C(13)	4*e*	0.0922(3)	0.8060(6)	0.1100(6)	0.064(3)	0.048(3)	0.079(3)	0.023(2)	0.023(2)	0.030(2)
C(14)	4*e*	0.1290(2)	0.8033(5)	0.2136(5)	0.057(3)	0.036(2)	0.077(3)	0.012(2)	0.025(2)	0.019(2)
C(15)	4*e*	0.1560(3)	0.9226(5)	0.2763(6)	0.073(3)	0.026(2)	0.095(3)	0.007(2)	0.036(3)	0.009(2)
C(16)	4*e*	0.1929(3)	0.9115(6)	0.3699(6)	0.068(3)	0.034(2)	0.093(3)	–0.009(2)	0.029(3)	–0.004(2)
C(17)	4*e*	0.2078(2)	0.7870(5)	0.4194(5)	0.052(2)	0.029(2)	0.077(3)	–0.006(2)	0.026(2)	–0.008(2)
C(18)	4*e*	0.2467(2)	0.7686(6)	0.5191(6)	0.055(3)	0.052(3)	0.081(3)	–0.020(2)	0.017(2)	–0.020(2)
C(19)	4*e*	0.2569(2)	0.6452(6)	0.5661(6)	0.047(3)	0.060(3)	0.073(3)	–0.013(2)	0.000(2)	–0.018(2)
C(20)	4*e*	0.2285(2)	0.5358(5)	0.5141(5)	0.044(2)	0.043(2)	0.061(3)	–0.007(2)	–0.002(2)	–0.005(2)
C(21)	4*e*	0.1814(2)	0.6668(5)	0.3697(5)	0.039(2)	0.026(2)	0.064(2)	–0.003(2)	0.017(2)	–0.002(2)
C(22)	4*e*	0.1434(2)	0.6766(5)	0.2647(5)	0.044(2)	0.026(2)	0.062(2)	0.007(2)	0.021(2)	0.008(2)
C(23)	4*e*	0.3346(3)	0.4278(8)	0.2802(7)	0.060(4)	0.101(5)	0.098(5)	–0.045(4)	–0.015(3)	–0.005(4)
N(1)	4*e*	0.1219(2)	0.5602(4)	0.2131(3)	0.036(2)	0.031(2)	0.045(2)	0.007(2)	0.004(2)	0.012(2)
N(2)	4*e*	0.1916(2)	0.5436(3)	0.4194(3)	0.038(2)	0.025(2)	0.048(2)	–0.003(2)	–0.001(2)	0.000(2)
N(3)	4*e*	0.3173(2)	0.1948(6)	0.3505(4)	0.029(2)	0.092(4)	0.064(3)	0.011(2)	0.002(2)	0.008(3)
O(1)	4*e*	0.2155(1)	0.2875(4)	0.2682(3)	0.028(2)	0.056(2)	0.051(2)	0.005(2)	0.006(1)	–0.008(2)
O(2)	4*e*	0.2468(2)	0.3160(5)	0.0785(3)	0.041(2)	0.097(3)	0.046(2)	–0.023(2)	–0.002(2)	0.002(2)
O(3)	4*e*	0.3653(2)	0.0166(6)	0.2407(6)	0.079(4)	0.123(5)	0.138(5)	0.020(3)	–0.023(3)	–0.062(4)
O(4)	4*e*	0.3444(2)	–0.0099(5)	0.4611(6)	0.053(3)	0.078(3)	0.170(5)	–0.004(2)	0.007(3)	0.036(3)
O(5)	4*e*	0.0899(1)	0.2505(3)	0.1963(2)	0.031(2)	0.040(2)	0.033(2)	–0.012(1)	0.003(1)	–0.008(1)
O(6)	4*e*	0.0175(1)	0.1253(3)	0.1362(3)	0.041(2)	0.054(2)	0.048(2)	–0.023(2)	0.003(2)	–0.018(2)
O(1W)	4*e*	0.1458(1)	0.2358(3)	0.4815(2)	0.033(2)	0.040(2)	0.035(2)	0.010(1)	0.004(1)	0.009(1)
O(2W)	4*e*	0.0598(1)	0.4261(3)	0.4103(3)	0.036(2)	0.036(2)	0.041(2)	0.014(1)	0.005(1)	0.004(1)
S(1)	4*e*	0.36075(6)	0.0725(2)	0.3595(2)	0.0377(8)	0.069(1)	0.094(1)	0.0008(7)	–0.0064(7)	–0.0124(9)

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References

1. Appleton, T. G.; Hall, J. R.; Prenzler, P. D.: Reaction of the *cis*-diammine-diaquaplatinum(II) Cation with *N*-acetylglycine. Inorg. Chem. **28** (1989) 815-819.
2. Sigel, H.; Martin, R. B.: Coordinating Properties of the Amide Bond. Stability and Structure of Metal Ion Complexes of Peptides and Related Ligands. Chem. Rev. **82** (1982) 385-426.
3. 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.
4. Wang, J. G.; Ma, L. F.; Wang, L. Y.; Wang, Y. H.; Liu, R.: Crystal structure of (1,10-phenanthroline)(*N*-tosyl-serinato)copper(II), $Cu(C_{12}H_8N_2)(C_{10}H_{11}NO_5S)$. Z. Kristallogr. NCS **220** (2005) 606-608.
5. Antolini, L.; Battaglia, L. P.; Corradi, A. B.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C.: α- and β-Carboxylic Groups as Primary Ligating Groups in Promoting Amide Deprotonation. Solid-state Behavior of *N*-Tosylalaninate-Copper(II) Complexes: Crystal and Molecular Structures of Bis(*N*-tosyl-*p*-alaninato)bis(imidazole)copper(II), Polymeric (*N*-Tosyl-α-alaninato)diaquacopper(II) Monohydrate, and Dipiperidinium Bis(*N*-tosyl-α-alaninato)cuprate(II) Monohydrate Complexes. J. Am. Chem. Soc. **107** (1985) 1369-1375.
6. Battaglia, L. P.; Bonamartini C. A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C.: Synthesis and Spectroscopic and Structural Properties of Bis(*N*-acetyl-DL-tryptophanato)copper(II) Complex and its Amine Adducts. Effect of Amines on the Amino Acid Coordination. Crystal and Molecular Structure of Diaquabis(*N*-acetyl-DL-tryptophanato)-bis(pyridine)copper(II). J. Am. Chem. Soc. **102** (1980) 2663-2669.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.